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INDUSTRIAL PULVERIZED COAL LOW-NO_x BURNER PHASE I
Final Report

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For
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Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts 02140-2390

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Executive Summary

Introduction

Increasingly tight limits have been placed on emissions of nitrogen oxides (NO_x) from combustion systems firing any fossil fuel. However, the problem of controlling NO_x emissions is especially difficult for fuels such as coal, which contain high levels of organically bound nitrogen. In conventional burners, a significant fraction of this fuel nitrogen can be converted to nitric oxide in the lean zone.

Arthur D. Little, Inc., jointly with its university partner, the Massachusetts Institute of Technology, and its industrial partner, Hauck Manufacturing Corporation, is developing a low NO_x pulverized coal burner for use in industrial processes, including those which may require preheated air or oxygen enrichment. The design of the burner specifically addresses the critical performance requirements of industrial systems, namely: high heat release rates, short flames, even heat flux distribution, and high combustion efficiency. The design is applicable to furnaces, industrial boilers, and cement kilns. The development program for this burner includes a feasibility analysis, performance modelling, development of the burner prototype design, and assessment of the economic viability of the burner.

U.S. industrial fossil fuel use in 1991 was approximately 20 quadrillion Btu (quads). Coal accounts for only approximately 13 percent of this, mostly in the cement industry, particularly in Pennsylvania, Texas, Utah, and California. Other industries operating a significant number of coal plants include chemicals, paper, food, and textiles. A large portion of the present industrial oil and gas fuel load could be taken up by coal if suitable low- NO_x burners with flame and combustion characteristics similar to those of current oil and gas burners were available.

The Phase I activities covered by this report consisted of three principal tasks:

- Preliminary burner design;
- Fluid flow/combustion modelling and analyses; and
- Market evaluation.

The preliminary design activities included the selection of a design coal for the Phase I design, preliminary design layout, and preliminary sizing of the burner components. Modelling and analysis were conducted for the coal pyrolysis zone, the rich combustion zone and the lean burnout zone. Both chemical kinetics analyses and one-dimensional coal combustion modelling were performed. The market evaluation included a review of existing industrial coal use, identification of potential near- and long-term markets and an assessment of the optimum burner sizes.

Burner Concept

The coal fired, low-NO_x burner has been designed for operation on pulverized coal with combustion air preheated up to 800K (950°F). The burner makes use of hot flue gas recirculation, staged combustion and reburning to achieve an anticipated NO_x emissions level of approximately 100 - 150 ppm. A schematic process flow diagram for the burner is shown in Figure S-1. The major features of the burner design are:

Jet Pump. The jet pump is driven by energy in the combustion air. The primary combustion air is accelerated through the jet pump nozzle, and the resulting jet entrains the surrounding gas, thereby recirculating flue gas from the furnace. It is designed to pull hot flue gas from an appropriate area of the furnace and pump the gas, which is mixed with pulverized coal and combustion air, through the burner into the furnace. The pump is designed to draw furnace gas at a temperature of up to 1400 K (2000°F) and a mass flow of up to 40 percent of the pump combustion air flow.

Volatilization Duct. Product gas from the furnace chamber or stack is designed to flow through an insulated conduit to the jet pump. Pulverized coal fed into the hot gas stream will undergo rapid heating and devolatilization. High recirculation rates of the product gas provide sufficient thermal energy for the pyrolysis of coal and aid in the conversion of the organically bound-nitrogen in coal to molecular nitrogen.

Combustion Staging. Combustion air is divided into primary and secondary streams. The primary combustion air is the driving fluid for the jet pump, and is mixed with the recirculated flue gas. Highly fuel-rich conditions in the primary combustion zone are maintained for sufficient time to promote evolution of a large fraction of fuel-bound nitrogen and promote conversion of this FBN to molecular nitrogen. In addition, NO present in the recirculated flue gas will be reduced by reburning reactions in the rich zone. A lean combustion zone is created in the furnace chamber by injection of secondary air and flue gas.

NO_x Control Strategy

Pyrolysis. Early pyrolysis of the pulverized coal is achieved by injecting the fuel into the hot recirculated flue gases. This approach provides early release of fuel nitrogen and consequently the maximum time for conversion of fixed nitrogen to molecular nitrogen in the rich combustion zone.

Flue Gas Recirculation. Flue gas recirculation has been found to be highly effective in reducing NO_x emissions. Various industrial burner manufacturers have reported significant NO_x emissions reductions (up to 60 - 70 percent) attributable to flue gas recirculation. The success of FGR can be attributed to three main phenomena: (1) flue gas serves as a diluent to the combustion process, causing reduction of the peak temperature in the flames; (2) FGR reduces the partial pressure of oxygen in the reactants, diminishing the oxidation potential for converting molecular nitrogen to

Figure S-1. Schematic process flow diagram for low-NO_x coal burner.

thermal NO_x ; and (3) FGR, under favorable fuel-rich conditions and high temperature, enables reburning of flue-gas-born NO_x to molecular nitrogen, thus adding another NO_x reduction pathway.

Air staging. The creation of fuel-rich and fuel-lean combustion zones in flames by means of staging the input of air or fuel is an established method of NO_x emission control. Air-staging is particularly suited to controlling NO_x emissions from combustion of fuels with significant fuel-bound nitrogen, such as coals. The degree of conversion of FBN to molecular nitrogen is determined by the thermodynamics of the system and by the rates of reactions in the fuel-rich flame zone. In practical combustion systems the reactions of FBN and NO may be kinetically constrained and the provision of adequate residence time and temperature in the rich zone is essential for high conversion of fixed nitrogen to molecular nitrogen. The rate of this conversion generally increases with increasing fuel equivalence ratio and temperature.

The objective, therefore, is to remove as much FBN from the coal as possible in the rich zone and convert it to molecular nitrogen so that little of the FBN is left in the char for subsequent conversion to thermal NO_x in the fuel-lean zone. The external air-staging in the burner concept serves to delay mixing of secondary combustion air and to allow maximum residence time in the rich zone for conversion of fuel nitrogen to molecular nitrogen.

Reburning. The process popularly termed reburning depends on hydrocarbon fragments such as CH_2 and CH rapidly reacting with NO to produce HCN and NH_3 in a secondary fuel-rich flame zone, with the latter species subsequently being converted to N_2 . This can take 100 ms or longer, depending on the temperature. In practical implementation the process is in reality a multiply-staged combustion process: lean-rich-lean. Advantage of this NO destruction pathway is taken in the proposed burner: NO in the recirculated flue gases is reduced to molecular nitrogen by these reburning reactions in the burner rich zone.

Modelling and Design Optimization

A review of data from the coal industry, coal and boiler/furnace trade associations, boiler/furnace operators, the Department of Energy, and the technical literature was made in order to select a set of coal characteristics to be used in the design analysis and modelling activities. A set of coal selection criteria was developed based on the program needs, DOE/PETC requirements, and U.S. industrial coal use patterns. Pittsburgh #8 coal was selected as the most appropriate fuel for the program. This coal is well characterized, available for purchase in small quantities for test purposes, and is representative of the coals used in U.S. industry.

Pyrolysis Zone

Several approaches were taken to determine the required pyrolysis conditions and timescales. Pyrolysis of Pittsburgh #8 coal has been studied by a number of workers and the reported data indicate that pyrolysis becomes strong at approximately 1100K (1500°F) and that the primary products are tars and heavy liquids. In order to achieve a minimum pyrolysis temperature of 1100K it is important ensure that the recirculated flue gas temperature is as high as possible and that the coal carrier mass flow is as low as possible. The preferred condition was 40 percent flue gas recirculation (based on the total burner mass flow) at a temperature of 1400K (2000°F) and a coal to carrier mass loading of at least 5:1.

In addition to review of the literature for Pittsburgh #8 coal, a proprietary pyrolysis code developed by Advanced Fuels Research (AFR) and a one-dimensional coal combustion code were both used to analyze the coal pyrolysis in the flue gas. The AFR code is a general mechanistic model which includes detailed chemistry, species evolution, and mass and heat transport. The one-dimensional coal combustion code pyrolysis model is based on an assumption of two competitive first-order reactions, each of which describes the degradation of coal to residual char and volatile fractions.

The pyrolysis timescales depend critically on the coal particle size distribution. In the analyses conducted to date, two size distributions have been considered: (1) a distribution corresponding to 90 percent through 200 mesh, i.e. close to utility pulverized coal grind, with a mass mean diameter (MMD) of $\sim 23 \mu\text{m}$ and 90 percent of the mass in particle smaller than $\sim 80 \mu\text{m}$; and (2) a fine coal with a MMD of $\sim 6 \mu\text{m}$ and 90 percent of the mass in particle smaller than $\sim 25 \mu\text{m}$. In the one-dimensional coal combustion model, each coal particle size distribution was modelled as a ten part stepwise function and the history of particles of each of the ten sizes was tracked, as well as the global gas phase chemistry and physical conditions.

Both models showed that pyrolysis in the flue gas for all conditions of interest produces essentially proximate volatile yields. The time required is on the order of 30 ms for a $30 \mu\text{m}$ coal particle: thus the fine coal pyrolysis is essentially complete after 30 ms, whereas the utility grind coal requires 80 - 90 ms to reach complete pyrolysis. The proportion of fuel nitrogen released roughly matches the fraction of carbon released. Thus pyrolysis in the flue gas releases approximately one third of the fuel nitrogen, primarily as HCN.

Rich Combustion Zone

The objective here is to rapidly mix the pyrolysis products and the primary combustion air in order to achieve fuel-rich combustion of the coal pyrolysis products at conditions which will promote the conversion of all of the fixed nitrogen to molecular nitrogen.

Kinetics Modelling. Chemical kinetics modelling of the fuel-rich reaction zone was performed to aid in defining optimum operating conditions to achieve the desired total fixed nitrogen (TFN) destruction. The kinetics modelling was performed using the latest versions of Sandia National Laboratory's CHEMKIN-II package.

Several simplifying assumptions have been made in order to address the problem of rich zone nitrogen control in the coal burner with the available kinetics tools. Two major difficulties are: (1) the lack of detailed mechanisms and kinetic parameters for oxidation of the heavy tars and liquids that evolve during the pyrolysis step; and (2) the inability to treat heterogeneous char oxidation properly. It is possible to make simplifying assumptions to overcome the above difficulties and yet allow the kinetics modelling objectives to be met. In order to estimate the temperatures, stoichiometries and residence times required to meet the TFN reduction objectives, equilibrium combustion products for two cases were considered as the starting point for the kinetics analysis: (a) the combustion in the primary air of just the coal pyrolysis products; and (b) combustion in the primary air of the pyrolysis products plus the char. The fate of various initial fixed nitrogen species in these combustion products was studied as a function of stoichiometry, temperature and time using a plug flow reactor (PFR) model. The detailed hydrocarbon oxidation and prompt, fuel and thermal nitrogen oxides mechanisms from the widely used Miller and Bowman (Sandia/Stanford) mechanism were used for these computations.

For a given stoichiometry, a higher reactor temperature is clearly beneficial. For example, an increase in temperature from 1900 K (2950°F) to 2000 K (3150°F) can reduce the time required for a 70 percent reduction in TFN from approximately 450 ms to approximately 150 ms. Several key conclusions were drawn from the kinetics analysis:

- For the case in which the char is not oxidized in the rich zone, the global stoichiometry must be extremely rich in order to achieve a gas-phase stoichiometry which is in the range needed for TFN destruction (approximately 1.3 - 1.9). For example, given typical volatile yields in the pyrolysis step (approximately 40 percent), a global fuel equivalence ratio of 3.4 is needed to achieve a gas-phase equivalence ratio of 1.4. Another consequence of this is that the maximum flame temperatures that can be achieved are very low - too low to give significant TFN destruction. Thus it is necessary to achieve significant char oxidation in the rich zone to generate high enough temperatures. This has an implication for the choice of fuel size.
- There is a conflict between the requirement of increased FGR for flame temperature suppression in the lean zone and the requirement for a high temperature in the rich zone for fixed nitrogen destruction. This leads us to consider introducing the recirculated flue gas into the secondary combustion air, rather than into the primary combustion air.

- Residence times of order 100 ms or greater are required for significant TFN destruction.

Subsequent chemical kinetics analysis of the rich zone assumed complete carbon conversion and release of all fuel nitrogen. A series of analyses led to the development of operating maps for the rich zone of the burner, indicating appropriate temperature/stoichiometry combinations required for a given level of TFN reduction in a specified residence time. These analyses indicated that it was possible to achieve over 90 percent reduction of the total fixed nitrogen present after all fuel nitrogen release.

One-Dimensional Coal Combustion Modelling. The one-dimensional coal combustion model was also used to examine fuel size effects in the rich zone. For the case of 40 percent flue gas recirculation and a 50/50 primary/secondary combustion air split, the total time required for a carbon conversion of more than 90 percent was over 200 ms for the utility grind coal and only 40 ms for the fine coal. Thus the utility grind coal combustion in the rich zone is too slow to either produce a rich enough gas-phase stoichiometry for long enough or to release all the fuel nitrogen. The fine coal cases considered to date show the potential for essentially complete carbon conversion and nitrogen release in a short enough time to subsequently allow significant conversion of fuel-bound nitrogen to molecular nitrogen.

Preliminary Burner Design

The key conclusions from the burner design analyses, which were incorporated into the burner preliminary design, are as follows:

- Coal particle entrainment, heatup and pyrolysis times are short. The coal lift line provides ample residence time and no additional dwell time need be provided between coal injection and the jet pump.
- A fine coal grind is required for rapid burnout in the rich zone, with complete release of fuel-bound nitrogen.
- If the coal is to be injected into the lift line, then the flue gas recirculation rate should be a maximum of 20 percent at 1400 K (2000°F), in order to maximize the temperature in the rich zone.
- If the coal is injected into the burner throat as opposed to being devolatilized by the recirculated flue gas, then the flue gas should be recirculated to the secondary combustion air to provide thermal NO_x control in the lean zone.
- Approximately 100 ms residence time should be provided in the rich zone. Additional rich zone residence time can be provided by delaying mixing of the secondary combustion air in the furnace.

- The primary/secondary airflow split should be approximately 50/50. The primary airflow will be adequate to entrain 20 percent flue gas.

The preliminary design for a 5 MM Btu/hr burner based on the above design principles is shown in Figure S-2.

Market Evaluation

We reviewed industrial coal-use databases to determine the US geographic distribution of industrial coal-fired boilers and furnaces and also the distribution of US coal use by industrial application. We then conducted interviews with representatives of industrial trade associations, coal companies, and industrial coal users to understand important issues for coal selection and use in specific industries. Many of the sources contacted during the review of industrial coal use also provided information useful for the market assessment. A number of additional trade associations were also contacted. Key factors driving the market for low-NO_x industrial pulverized coal burners are (1) State and Federal emissions regulations; and (2) the projected post-2000 increase in cost differential between coal and gas/oil. The latter will make coal a more attractive fuel, despite its additional emissions control requirements. Those installations which do not require supplemental sulfur and particulate control equipment will likely be the first to adopt the low-NO_x coal burner, followed by larger installations which need sulfur and particulate control equipment (because of economies of scale), and subsequently by smaller installations.

There is greatest potential for application of the low-NO_x burner in four areas: lime kilns, cement kilns, brick kilns and industrial boilers. Lime and cement kiln applications will require no additional flue gas desulfurization equipment, given the SO₂ capture inherent to the processes. In addition, most of the kilns in the country are already coal-fired. The near term market would be for lime kilns, with burners in the range 50 - 100 MM Btu/hr. The burner can then be scaled up for cement kilns (100 - 250 MM Btu/hr).

In the longer term the burner can be scaled up for larger industrial boilers, i.e. those which already burn coal and/or those in which the economic impact of SO₂ control will cause least hardship. The longest term market will be for small scale industrial boilers, where the relatively higher cost of FGD equipment will dictate a higher fuel price differential before switching to coal is attractive.

Conclusions

Preliminary design analyses and modelling have been completed for a low-NO_x pulverized coal burner. The burner design incorporates three proven NO_x control strategies: air staging; flue gas recirculation; and reburning. Detailed modelling has been performed using one-dimensional coal pyrolysis and combustion models and chemical kinetics models.

Figure S-2. Preliminary design for a 5 MM Btu/hr industrial PC low-NO_x burner (all dimensions in inches).

The principal conclusion from this preliminary design and analysis study is that NO_x emissions of below 0.2 lb/MM Btu can indeed be achieved when burning coals with significant fixed nitrogen contents.

The analyses performed to date indicate the importance of using a fine coal grind, in order to achieve rapid and essentially complete carbon conversion and fuel nitrogen evolution in the rich zone. A commercially available grind with a mass mean diameter of ~6 μm and 90 percent of the mass in particle smaller than ~25 μm appears appropriate. There are indications that for the coal burner, flue gas recirculation may be more appropriate in the secondary combustion air rather than in the primary combustion air, given the conflicting requirements of (1) increased flue gas recirculation for flame temperature suppression in the lean zone and (2) high temperature in the rich zone for fixed nitrogen destruction. Residence times in the rich zone of approximately 100 ms are required to achieve significant fixed nitrogen reduction.

A preliminary design for a 5 MM Btu/hr industrial pulverized coal burner has been prepared based on the guidelines that resulted from the design analyses. This burner is expected to achieve NO_x emissions of approximately 100 - 150 ppm at 3% O₂.

1 Introduction

1.1 Background

U.S. industrial fossil fuel use in 1991 was approximately 20 quadrillion Btu (Quads). Coal accounts for only approximately 13 percent of this, mostly in the cement industry, particularly in Pennsylvania, Texas, Utah, and California. Other industries operating a significant number of coal plants include chemicals, paper, food, and textiles. A large portion of the industrial oil and gas fuel load could be taken up by coal if suitable low-NO_x burners with flame and combustion characteristics similar to current oil and gas burners were available.

It is well known that both sulfur oxides (SO_x) and nitrogen oxides (NO_x) contribute to the formation of acid rain. NO_x has also been linked to the formation of ground-level ozone (and consequently to poor air quality in urban areas) and also to the destruction of the Earth's upper atmosphere ozone layer. Increasingly tight limits have therefore been placed on emissions of nitrogen oxides from combustion systems firing any fossil fuel.

The problem of controlling NO_x emissions is especially difficult for fuels such as coal, which contain high levels of organically bound nitrogen. In conventional burners, a significant fraction of this fuel nitrogen can be converted to nitric oxide in the lean combustion zone. Operation with preheated combustion air can also exacerbate the emissions of NO_x, because of higher flame temperatures.

Techniques for effective reduction of NO_x emissions from industrial burners include:

- Combustion process modifications (staged air or staged fuel injection, flue gas recirculation, and reburning); and
- Post-combustion control (selective catalytic reduction and selective non-catalytic reduction).

Post-combustion NO_x control technologies are well established commercial technologies, but are expensive to implement, operate and maintain. Combustion modification is a preferable NO_x-control option, both from an economic and operational perspective.

1.2 Objective

The objective of Phase I of the "Industrial Pulverized Coal Low-NO_x Burner" program is to develop a preliminary design for a novel, low-NO_x, pulverized coal burner which:

- Offers near-term commercialization potential;
- Uses preheated combustion air at up to 1000°F; and

- Can be applied to high temperature industrial heating furnaces, chemical process furnaces, fired heaters and boilers.

The program team is led by Arthur D. Little, Inc. (ADL), and includes the Massachusetts Institute of Technology (MIT), and Hauck Manufacturing Company (Hauck). The responsibilities of the various team members are as follows:

- **Arthur D. Little**
Overall project leadership
Burner concept definition
Combustion modelling
Engineering design
System integration
Field testing
- **Massachusetts Institute of Technology**
Analytical modelling
Burner concept definition
Burner design
Prototype burner testing
Data analysis
- **Hauck Manufacturing Company**
Engineering design
Manufacturing support services
Marketing/commercialization
Field demonstration

1.3 Phase I Activities

The Phase I activities consisted of three principal tasks:

- Preliminary burner design;
- Fluid flow/combustion modelling and analyses; and
- Market evaluation.

The preliminary design activities included the selection of a design coal for the Phase I design, preliminary design layout, and preliminary sizing of the burner components. Modelling and analysis were conducted for the coal pyrolysis zone, the rich combustion zone and the lean burnout zone. Both chemical kinetics analyses and one-dimensional coal combustion modelling were performed. The market evaluation included a review of existing industrial coal use, identification of potential near- and long-term markets and an assessment of the optimum burner sizes.

2 Burner Concept

2.1 Burner Arrangement

The novel industrial pulverized coal burner being developed by the team makes use of three proven NO_x -control approaches:

- Hot flue gas recirculation;
- Staged-air combustion; and
- Reburning.

It is anticipated that optimization of the burner design incorporating these three approaches can lead to NO_x emission levels of approximately 100 - 150 ppm. The coal fired, low- NO_x burner is intended for operation on pulverized coal with combustion air preheated up to 800 K (950°F).

A schematic process flow diagram for the burner is shown in Figure 2-1. The major components of the burner are:

Jet Pump. The jet pump is driven by energy in the combustion air. The primary combustion air is accelerated through the jet pump nozzle, and the resulting jet entrains the surrounding gas, thereby recirculating flue gas from the furnace. It is designed to pull hot flue gas from an appropriate area of the furnace and pump the gas, which is mixed with pulverized coal and combustion air, through the burner into the furnace. The pump is designed to draw furnace gas at a temperature of up to 1400 K (2000°F) and a mass flow of up to 40 percent of the pump combustion air flow.

Volatilization Duct. Product gas from the furnace chamber or stack is designed to flow through an insulated conduit to the jet pump. Pulverized coal fed into the hot gas stream will undergo rapid heating and devolatilization. High recirculation rates of the product gas provide sufficient thermal energy for the pyrolysis of coal and aid in the conversion of the organically bound-nitrogen in coal to molecular nitrogen.

Combustion Staging. Combustion air is divided into primary and secondary streams. The primary combustion air is the driving fluid for the jet pump, and is mixed with the recirculated flue gas. Highly fuel-rich conditions in the primary combustion zone are maintained for sufficient time to promote evolution of a large fraction of fuel-bound nitrogen (FBN) and promote conversion of this FBN to molecular nitrogen. In addition, NO present in the recirculated flue gas will be reduced by reburning reactions in the rich zone. A lean combustion zone is created in the furnace chamber by injection of secondary air and flue gas.

Figure 2-1. Schematic process flow diagram for low-NO_x coal burner.

2.2 NO_x Control Strategy

Pyrolysis. Early pyrolysis of the pulverized coal is achieved by injecting the fuel into the hot recirculated flue gases. This approach provides early release of fuel nitrogen and consequently the maximum time for conversion of fixed nitrogen to molecular nitrogen in the rich combustion zone.

Flue Gas Recirculation. Flue gas recirculation has been found to be highly effective in reducing NO_x emissions. Various industrial burner manufacturers have reported significant NO_x emissions reductions (up to 60 - 70 percent) attributable to flue gas recirculation. The success of FGR can be attributed to three main phenomena:

- Flue gas serves as a diluent to the combustion process, causing reduction of the peak temperature in the flames;
- FGR reduces the partial pressure of oxygen in the reactants, diminishing the oxidation potential for converting molecular nitrogen to thermal NO_x; and
- FGR, under favorable fuel-rich conditions and high temperature, enables reburning of flue-gas-born NO_x to molecular nitrogen, thus adding another NO_x reduction pathway.

Air staging. The creation of fuel-rich and fuel-lean combustion zones in flames by means of staging the input of air or fuel is an established method of NO_x emission control. Air-staging is particularly suited to controlling NO_x emissions from combustion of fuels with significant fuel-bound nitrogen, such as coals. The degree of conversion of FBN to molecular nitrogen is determined by the thermodynamics of the system and by the rates of reactions in the fuel-rich flame zone. In practical combustion systems the reactions of FBN and NO may be kinetically constrained and the provision of adequate residence time and temperature in the rich zone is essential for high conversion of fixed nitrogen to molecular nitrogen. The rate of this conversion generally increases with increasing fuel equivalence ratio and temperature.

The objective, therefore, is to remove as much FBN from the coal as possible in the rich zone and convert it to molecular nitrogen so that little of the FBN is left in the char for subsequent conversion to thermal NO_x in the fuel-lean zone. The external air-staging in the burner concept serves to delay mixing of secondary combustion air and to allow maximum residence time in the rich zone for conversion of fuel nitrogen to molecular nitrogen.

Reburning. The process popularly termed reburning depends on hydrocarbon fragments such as CH₂ and CH rapidly reacting with NO to produce HCN and NH₃ in a secondary fuel-rich flame zone, with the latter species subsequently being converted to N₂. This can take 100 ms or longer, depending on the temperature. In

practical implementation the process is in reality a multiply-staged combustion process: lean-rich-lean. Advantage of this NO destruction pathway is taken in the proposed burner: NO in the recirculated flue gases is reduced to molecular nitrogen by these reburning reactions in the burner rich zone.

2.3 Nominal Operating Conditions

The nominal operating parameters for the burner are listed in Table 2-1 below.

Table 2-1. Nominal Operating Parameters for Industrial PC Burner

Parameter	Value
Thermal input	5 MMBtu/hr
Fuel	Pittsburgh #8 Coal
Flue gas recirculation temperature	1100 - 1400 K (1500 - 2000°F)
Flue gas recirculation rate (percent of total flow)	20 - 40%
Flue gas O ₂ concentration	3%
Air preheat temperature	720 K (800°F)

3 Coal Selection

3.1 Introduction

3.1.1 Objective

The principal objective of the coal selection task was to choose a set of coal characteristics for use in the development of the burner design and in the combustion and NO_x-control modelling work. It is important that the coals used be well characterized and representative of "typical" industrial coals. We also identified coal seams and coal grinding facilities from which pulverized coal samples could be obtained for future burner test activities. Supporting objectives were:

- To develop a set of coal selection criteria for burner/design modelling activities;
- To identify US industries currently burning coal, determine their locations, business applications, and typical coals used;
- To identify a set of US coals that meet the selection criteria; and
- To identify facilities capable of grinding coal in two to ten ton batches for future low-NO_x burner testing.

3.1.2 Approach

Data were gathered and analyzed from the coal industry, coal and boiler/furnace trade associations, boiler/furnace operators, DOE, and technical literature on pulverized coal combustion and NO_x control. A set of coal selection criteria were developed based on program needs, DOE/PETC requirements, and US industrial coal use patterns. The approach used was as follows:

- Review industrial coal-use databases to determine the US geographic distribution of industrial coal-fired boilers and furnaces and the distribution of US coal use by industrial application;
- Interviews with representatives of industrial trade associations, coal companies, and industrial coal users to understand important issues for coal selection and use in industry;
- Review of DOE PETC requirements/interests for coal selection, such as compatibility of coal selection with parallel DOE-sponsored combustion modeling activities, and consistency of coal selection among other burner development contractors;
- Literature review of fundamental coal pyrolysis/char combustion/NO_x formation studies to assess the availability of kinetic information for targeted U.S. coals; and

- Review of U.S. coal seams to identify coals that meet the selection criteria developed in the previous tasks.

3.1.3 Selection Criteria

The following criteria were considered important to the selection of coal properties for the combustion modeling and burner design tasks. They are listed in order of importance to the program.

- The properties of the coal used should be typical of coals used in common U.S. industrial applications;
- The coal(s) selected should be characterized in enough detail (in the literature) that their combustion characteristics can be modeled with existing pyrolysis/char combustion correlations;
- The coal properties should be consistent with those of coals available for purchase in small quantities for (future) combustion tests at the MIT Combustion Research Facility; and
- The coal(s) should be typical of those used in recent or ongoing burner development work (sponsored by DOE or industry) so that the results of these programs are comparable.

3.2 Industrial Coal Use

3.2.1 Sources of Information

A variety of sources were contacted to gather the required information. The sources contacted included trade associations, coal companies, coal database services, industrial coal users, grinding facilities, and DOE PETC. These sources are listed in Table 3-1 below.

3.2.2 Current Coal Use in Industry

Figure 3-1 shows the distribution of U.S. industrial coal-fired boilers/furnaces. These coal fired systems include all boiler types, such as stoker fired boilers, pulverized coal boilers, and fluidized bed boilers. They also include furnaces such as cement kilns. This map shows that the states with the highest industrial coal-use are Ohio and Pennsylvania. In Ohio, there are a total of 91 industrial combustors (other than coke plants) that operate on coal. In Pennsylvania there are 60 industrial facilities burning coal. Other states with high industrial coal usage include Michigan (59 facilities), Illinois (37 facilities), Tennessee (31 facilities) and Kentucky (34 facilities). All these states have regions of non-attainment of National Ambient Air

Distribution of U.S. Industrial, Coal-Fired Boilers/Furnaces

Figure 3-1. Distribution of U.S. industrial coal-fired boilers and furnaces.

Table 3-1. Sources Contacted for Coal Selection Information

Group	Sources
Trade Associations	<ul style="list-style-type: none"> • CIBO (Council of Industrial Boiler Operators) • Portland Cement Association • National Coal Association
Coal Sales	<ul style="list-style-type: none"> • AMAX Coal Sales • Consolidated Coal
Coal Database Services	<ul style="list-style-type: none"> • Keystone Coal Manual • Resource Data International • Energy Information Agency
Industrial Coal Users	<ul style="list-style-type: none"> • Kaiser Cement, CA • PMC, Inc. (Chemicals), OH • Emory Chemicals, OH • Archer Daniels Midland (Food Processing), IL • Campbell's Soup, OH
Grinding Facilities	<ul style="list-style-type: none"> • ABB/Combustion Engineering • Resource Engineering, Inc. • Microfuels, Corp.
DOE	<ul style="list-style-type: none"> • Clifford Smith, PETC

Quality Standards (NAAQS) for ozone or NO_x , indicating that expansion of coal use in these states may be limited by NO_x emissions from existing and/or new facilities. The total number of industrial coal-fired units (excluding coke plants) in the U.S. is about 830.

The data in this map comes from the Energy Information Agency Form 3, a mailing list of manufacturing facilities (excluding coke plants) burning more than 1000 tons/year of coal. This data provides insight to areas of coal use in general and areas of potential expansion of coal use in the future. These numbers do not correspond directly for potential markets for the low- NO_x burner under development since some of the boiler/furnace geometries are incompatible with retrofit pulverized coal-fired burners (e.g. fluidized bed boilers or some stoker boilers).

Figure 3-2 shows the distribution of coal use by industry type. The largest percentage of coal-fired facilities in U.S. industry is in the combined industrial sector of stone, clay, concrete and glass manufacture/processing. This usage is dominated by the cement industry, which uses coal to fire kilns in Portland cement plants. Other

Figure 3-2. Distribution of U.S. industrial coal use by industry type.

industries operating significant numbers of coal plants include: Chemicals, Paper, Food and Textiles. The data presented were also derived from the EIA Form 3.

The distribution of Portland cement plants in the US is shown in Figure 3-3. There are large numbers of coal-fired cement plants in Pennsylvania, Texas, Utah and California. All of these states have regions in non-attainment of NAAQS for ozone or NO_x . Most California coal-fired cement kilns operate on Utah bituminous coal.

Interviews with coal sales and coal use representatives indicated that coal selection in U.S. industry is based on delivered coal price. The price of the coal is determined by both the coal cost (FOB mine) and the coal transportation cost. Therefore, coal users tend to use local coals to minimize transportation costs. In some cases, coal selection is limited by access to rail lines between mine and user site thereby limiting a boiler operator's choice in coals. Industrial coals are typically bituminous.

Coal ash and sulfur contents of industrial coals vary widely by application. Generally, however, the coal ash content is roughly 8 - 12%; the sulfur content can vary from 0.8 to 4.5%. The nitrogen content of bituminous coal ranges from 1.2 to 1.8%.

In the cement industry, coal properties vary widely by site. Kilns can take high or low sulfur coals depending on the necessary chemical balance for the cement manufacture. Generally, higher volatile contents (>20%) are desired for kiln applications. Kilns typically run on highly preheated combustion air (from recuperated heat), with secondary air temperatures up to 2000°F. The cement plants contacted indicated a need for NO_x controls on existing and future facilities.

The analysis of U.S. industrial coal use indicated that there is no "typical" industrial coal. However, it did indicate that coal use is driven by price and that local coals are frequently selected for cost effectiveness. Therefore, coals from Pennsylvania and Ohio may be candidate coals for selection for this low NO_x burner development program, since these states have the most coal-fired industrial facilities in the U.S. It is likely that many coal-fired industries in Michigan (another state with large numbers of coal-fired industrial boilers/furnaces) would use coal from these states as well. Alternatively, bituminous coals from Utah, representing the coal used in the cement industries in California and Utah, may provide a useful alternative coal.

3.3 Availability of Combustion Data

A brief literature review of coal pyrolysis and char combustion work was conducted to determine what coals have been used in fundamental experimental studies of coal combustion and/or NO_x formation. It is important to select a coal that is characterized well enough to facilitate modelling of coal pyrolysis, NO_x formation, and char combustion mechanisms in the low- NO_x burner. Table 3-2 below summarizes the papers reviewed and the coals included in these studies.

Figure 3-3. Distribution of coal-fired Portland cement plants in the U.S.

Table 3-2. Coal Combustion Papers Reviewed

Topic	Reference	Coals Studied
Coal Pyrolysis	Kobayashi, Howard and Sarofim	<ul style="list-style-type: none"> • Montana lignite-A (Savage mine) • Pittsburgh #8 hvA
	Ubhayakar, Stickler, von Rosenberg and Gannon	<ul style="list-style-type: none"> • Pittsburgh Seam bituminous
	Suuberg, Peters and Howard	<ul style="list-style-type: none"> • Montana lignite-A (Savage mine) • Pittsburgh #8 hvA
	Anthony, Howard, Hottel and Meissner	<ul style="list-style-type: none"> • Montana lignite-A (Savage mine) • Pittsburgh #8 hvA
Char Combustion	Hurt and Hardesty	<ul style="list-style-type: none"> • PETC Suite of Coals: <ul style="list-style-type: none"> - Lower Kittanning lvb - Pocahontas #3 lvb - Pittsburgh #8 hvb - Illinois #6 hvb - Utah hvb - Dietz subbituminous - Lower Wilcox lignite
	Lester, Seeker and Merklin	<ul style="list-style-type: none"> • Pittsburgh Seam bit. • Illinois #6
	Laurendeau	<ul style="list-style-type: none"> • Various (review paper)
	Smith	<ul style="list-style-type: none"> • New Zealand bituminous
NO _x Formation	Pohl and Sarofim	<ul style="list-style-type: none"> • Montana lignite-A (Savage mine) • Pittsburgh #8 hvA
	Glass and Wendt	<ul style="list-style-type: none"> • Utah bituminous
	Pershing and Wendt	<ul style="list-style-type: none"> • Colorado • Pittsburgh #8 • Western Kentucky • Montana subbit
	Wendt, Pershing, Lee and Glass	<ul style="list-style-type: none"> • Western Kentucky

The coals of interest repeatedly referenced in these papers include the Pittsburgh Seam coals, specifically Pittsburgh #8. This is a medium to high volatile bituminous coal with ash content of 8 - 10%, moisture of 2 - 5% and sulfur content of 1.5 - 3.5%. There are some studies that include work with Utah bituminous coals, which are also of interest to this program because of its use in the Cement industry in California and Utah.

3.4 Design Coal Selection

On the basis of the above review, the following coals adequately meet the requirements of the project:

- Pittsburgh Seam Bituminous
- Pittsburgh #8
- Utah Bituminous Coals (Castlegate, Sunnyside)

All of these coals are well characterized, are available for purchase in small quantities and are representative of coals used by U.S. industry. The Pittsburgh #8 seam is mined both in Pennsylvania and Ohio. In fact, almost 20% of total Ohio coal production is from the Pittsburgh #8 seam. Pittsburgh Seam coal also provides about 25% of the total Pennsylvania coal production. It is produced almost entirely from very large underground mines.

After review by the program team, Pittsburgh #8 was selected as the design coal for the project. The properties of the design coal are listed in Table 3-3.

Table 3-3. Physical Properties of Pittsburgh #8 Coal

Parameter	Value
Nominal Size	30 micron mean particle size
Volatile Content	> 35 wt percent
Heating Value	13,000 Btu/lb
Ash Content	< 5 wt percent
Moisture Content	< 3 wt percent
Swelling Index	Low
Fuel-bound Nitrogen	1.4 wt percent
Availability	Several sources

4 Burner Design Analyses

4.1 Pyrolysis Zone

Pyrolysis data for Pittsburgh #8 coal available in the literature include those obtained by Suuberg et al. (1978), Solomon et al. (1982) and Solomon et al. (1990). In addition to previously reported data, a proprietary computer code developed by Advanced Fuel Research (AFR) was used by MIT to obtain pyrolysis timescales and product distributions. The AFR code (Solomon, 1990) is a general mechanistic model which includes detailed chemistry, species evolution, and mass and heat transport and has been developed over many years.

Key conclusions of the MIT work were that:

- Recirculated flue gas should be at a temperature of at least 1400 K (2000°F) and no less than 20 percent of the total flow, in order to achieve a minimum pyrolysis temperature of 1100 K (1500°F).
- For a 30 μm coal particle, the entrainment time will be 2 ms, particle heatup time will be 10 ms, and the pyrolysis will be complete in 15 ms.

The MIT analysis using the AFR code considered only coal particles of 30 μm diameter. A one-dimensional coal combustion model based on the work of Stickler et al. (1979) and Ubhayakar et al. (1977) was also used to evaluate the pyrolysis of representative coal particle size distributions. The one-dimensional coal combustion code pyrolysis model is based on an assumption of two competitive first-order reactions, each of which describes the degradation of coal to residual char and volatile fractions.

Pyrolysis timescales depend critically on the coal particle size distribution. Two size distributions were evaluated using the one-dimensional combustion code. The input coal particle size distributions are shown in Figure 4-1. The larger size distribution (90% -200 mesh) is designated the "Reference Coal" and is close to a conventional utility power plant pulverized coal grind. It has a mass mean diameter (MMD) of 23 μm and 90 percent of the mass is in particles smaller than $\sim 80 \mu\text{m}$. The smaller size distribution is designated the "Fine Coal" and is that of a commercially available fine coal grind. It has a MMD of 6 μm and 90 percent of the mass in particles smaller than $\sim 25 \mu\text{m}$.

Each coal particle size distribution was modelled as a ten part stepwise function. For example, the 90% -200 mesh reference coal particle distribution was divided between the sizes 4, 7, 10, 13, 22, 32, 40, 52, 90, and 130 μm . The temperature, size and composition history of particles of each of the ten sizes was then tracked, as was the global solid and gas phase chemistry and physical conditions.

Figure 4-1. Coal particle size distributions used in coal combustion model.

Table 4-1. Pyrolysis Cases Computed Using One-Dimensional Combustion Model

Case	Coal Size	Flue Gas Recirculation Rate (%)	Flue Gas Temperature K
A1	Ref (MMD 23 μm)	40	1100
A2	Ref (MMD 23 μm)	20	1400
A3	Ref (MMD 23 μm)	40	1400
A4	Fine (MMD 6 μm)	40	1400
A5	Fine (MMD 6 μm)	40	1100

Five pyrolysis cases were computed, as detailed in Table 4-1. In all cases, the following assumptions were made:

Coal type	Pittsburgh #8
Flue gas O_2	3%
Coal loading ratio (coal:air)	5:1
Coal and carrier temperature	400 K (200°F)

A sample output plot from the model is shown in Figure 4-2. Results of the computations for each of the above cases are provided in Appendix A. Each of these output plots consists of four charts. The upper left chart shows global parameters as a function of time, including the following:

Fraction of carbon gasified (Cgas)	Green line
Fraction of hydrogen gasified (Hgas)	Dark blue line
Mixture temperature (C Gas T)	Red line

The upper right chart indicates the temperature histories of the various particle sizes. The first knee in the temperature history curves indicates the change from particle heat-up and drying to volatile evolution. The second knee in the temperature histories indicates the change from pyrolysis to much slower heterogeneous char oxidation.

The lower right plot shows the normalized particle masses as a function of time. Once again the sequence of drying, devolatilization and char oxidation is clearly visible as a function of particle size.

Finally, the lower left plot shows global gas phase chemistry as a function of time. The oxygen (present in the carrier and flue gas) is depleted very rapidly and the gas phase chemistry reaches steady state after approximately 50 msec.

Case A3

Figure 4-2. Sample output from one-dimensional coal combustion model for pyrolysis zone.

Table 4-2. Results of Pyrolysis Computations

Case	Coal Size	Flue Gas Recirculation Rate (%)	Flue Gas Temperature K	Approximate time to achieve 95% pyrolysis (ms)
A1	Ref (MMD 23 μ m)	40	1100	200
A2	Ref (MMD 23 μ m)	20	1400	140
A3	Ref (MMD 23 μ m)	40	1400	80
A4	Fine (MMD 6 μ m)	40	1400	30
A5	Fine (MMD 6 μ m)	40	1100	50

To first order, the degree of hydrogen gasification (H_{gas}) indicates the degree of completeness of pyrolysis. The times to achieve 95 percent hydrogen gasification are given in Table 4-2. These times include a characteristic coal/carrier/flue gas mixing time of 20 ms (based on pipe diameter and gas velocities). As expected, the shortest pyrolysis times are for the fine coal with the highest flue gas temperature and the longest are for the reference coal with the lowest temperature flue gas. The indicated timescales for a 30 μ m particle agree well with those computed by MIT. However, the importance of the coal grind in ensuring complete pyrolysis in less than 50 ms is clear. Essentially proximate volatile yield was calculated for almost all flue gas recirculation rates and temperatures of interest.

4.2 Rich Combustion Zone

The creation of fuel-rich and fuel-lean combustion zones in flames by means of staging the input of air or fuel is an established method of NO_x emission control. Air-staging is particularly suited to controlling NO_x emissions from combustion of fuels with significant fuel-bound nitrogen, such as coals. The degree of conversion of FBN to molecular nitrogen is determined by the thermodynamics of the system and by the rates of reactions in the fuel-rich flame zone. In practical combustion systems the reactions of FBN and NO may be kinetically constrained. Therefore the provision of adequate residence time and temperature in the rich zone is essential for high conversion of fixed nitrogen to molecular nitrogen. The rate of this conversion generally increases with increasing fuel equivalence ratio and temperature.

The objective, therefore, is to remove as much FBN from the coal as possible in the rich zone and convert it to molecular nitrogen so that little of the FBN is left in the char for subsequent conversion to thermal NO_x in the fuel-lean zone. The external

air-staging in the burner concept serves to delay mixing of secondary combustion air and to allow maximum residence time in the rich zone for conversion of fuel nitrogen to molecular nitrogen.

4.2.1 Kinetics Modelling

Chemical kinetics modelling of the fuel-rich reaction zone was performed to aid in defining optimum operating conditions to achieve the desired total fixed nitrogen (TFN) destruction. The kinetics modelling was performed using the latest versions of Sandia National Laboratory's Chemkin-II package (Kee et al., 1991).

Approach. Several simplifying assumptions have been made in order to address the problem of rich zone nitrogen control in the coal burner with the available kinetics tools. Two major difficulties are: (1) the lack of detailed mechanisms and kinetic parameters for oxidation of the heavy tars and liquids that evolve during the pyrolysis step; and (2) the inability to treat heterogeneous char oxidation properly. It is possible to make simplifying assumptions to overcome the above difficulties and yet allow the kinetics modelling objectives to be met. In order to estimate the temperatures, stoichiometries and residence times required to meet the TFN reduction objectives, two different equilibrium combustion products were assumed as the starting point for the kinetics analysis: (a) the combustion in the primary air of just the coal pyrolysis products; and (b) combustion in the primary air of the pyrolysis products plus the char. The fate of various initial fixed nitrogen species in these combustion products was studied as a function of stoichiometry, temperature and time using a plug flow reactor (PFR) model. The comprehensive hydrocarbon and NO_x mechanisms of Miller and Bowman (1989) were used for these computations. The detailed reaction mechanism is presented in Appendix F.

Initial Results. Typical results from this analysis are shown in Figure 4-3. In this figure, the mole fractions of various nitrogenous species are plotted as a function of residence time in the PFR. In this case, the initially high concentration of HCN declines rapidly, from several hundred ppm to less than 1 ppm in approximately 100 ms. The result is a reduction in TFN of approximately 80 percent in the PFR (or rich combustion zone). Many such analyses were conducted, for various initial stoichiometries, temperatures, flue gas conditions, and assumptions regarding the char combustion. Figure 4-4 shows the results of similar analyses, and indicates the effect of reactor (or rich zone) temperature on the reduction of total fixed nitrogen. For a given stoichiometry, a higher reactor temperature is clearly beneficial. For example, an increase in temperature from 1900 K (2950°F) to 2000 K (3150°F) can reduce the time required for a 70 percent reduction in TFN from approximately 450 ms to approximately 150 ms.

Figure 4-5 shows a compilation of such TFN reduction calculations. In this chart the adiabatic flame temperatures for various primary zone combustion conditions are plotted against the rich zone fuel-air equivalence ratio. Also plotted are several lines marking temperature-equivalence ratio combinations that will achieve a certain level

Figure 4-3. Results of typical CHEMKIN analysis: concentrations of various fixed nitrogen species as a function of time in the plug flow reactor.

Figure 4-4. Effect of reactor temperature on total fixed nitrogen in the plug flow reactor.

TFN1

Figure 4-5. Results of initial kinetics study: adiabatic flame temperatures for various conditions (symbols) and contours of 70% TFN reduction for various times (no symbols).

(in this case, 70 percent) of fixed nitrogen reduction for various rich-zone residence times (100, 200, and 350 ms). Three sets of adiabatic flame temperature calculations are presented: two cases in which the char is completely oxidized in the fuel-rich zone ("all coal reacts," 40 and 20 percent flue gas recirculation); and one case in which the char is not oxidized, and simply acts as an inert heat sink ("volatiles react," 40 percent flue gas recirculation). These two assumptions help to bracket the problem of properly dealing with heterogeneous char oxidation in Chemkin. Three key points may be made concerning Figure 4-5 and the initial Chemkin results:

- (1) For the case in which the char is not oxidized in the rich zone, the global stoichiometry must be extremely rich in order to achieve a *gas-phase* stoichiometry which is in the range needed for TFN destruction (approximately 1.3 - 1.9). For example, given typical volatile yields in the pyrolysis step (approximately 40 percent), a global fuel equivalence ratio of 3.4 is needed to achieve a gas-phase equivalence ratio of 1.4. This requires an impractical primary/secondary combustion air split of 20/80. Another consequence of this is that the maximum flame temperatures that can be achieved are very low - too low to give significant TFN destruction. This can be seen from the adiabatic flame temperature curve for the "volatiles react" case. Thus it is necessary to achieve significant char oxidation in the rich zone to generate high enough temperatures. This has an implication for the choice of fuel size.
- (2) There is a conflict between the requirement of increased FGR for flame temperature suppression in the lean zone and the requirement for a high temperature in the rich zone for fixed nitrogen destruction. This leads us to consider introducing the recirculated flue gas into the secondary combustion air, rather than into the primary combustion air.
- (3) Significant residence times, of order 100 ms, are required for significant TFN destruction.

Rich Zone Design Analysis. Given that it is necessary to obtain essentially complete coal combustion in the rich zone in order to generate gas-phase equivalence ratios and temperatures conducive to TFN destruction, kinetics calculations were performed for such a scenario. Effects of stoichiometry, temperature and residence time were explored in order to determine which operating conditions would best achieve the program NO_x reduction goals, given that essentially all the coal nitrogen will be released in the rich zone. If all the coal nitrogen is released in the rich zone, this will give a total fixed nitrogen concentration of approximately 2000 ppm.

The results of this analysis are best presented as a burner "operating map" for rich-zone total fixed nitrogen (TFN) reduction, similar to that shown in Figure 4-5. Three such maps are shown in Figures 4-6 - 4-8, for rich zone residence times of 50, 100 and 200 ms, respectively. A complete set of operating maps is provided in Appendix B.

Figure 4-6. Adiabatic flame temperatures and contours of TFN reduction for 50 ms residence time in rich zone assuming complete carbon conversion.

Figure 4-7. Adiabatic flame temperatures and contours of TFN reduction for 100 ms residence time in rich zone assuming complete carbon conversion.

Figure 4-8. Adiabatic flame temperatures and contours of TFN reduction for 200 ms residence time in rich zone assuming complete carbon conversion.

FIG 4-8

In Figures 4-6 - 4-8, the adiabatic plug flow reactor temperature is plotted against the reactor fuel-air equivalence ratio for various air flow splits and for three cases: 40 percent flue gas recirculation (FGR) with a flue gas temperature of 1400K (2000°F); 20 percent FGR at 1400K; and no FGR. Also plotted are several lines marking temperature-equivalence ratio combinations that will achieve a given percentage fixed nitrogen reduction for given reactor residence times.

Approximately 90 percent TFN reduction in the rich zone is expected to result in 100 - 150 ppm NO at the furnace exit (excluding thermal NO_x generation in the lean zone). It can be seen from Figure 4-6 that for a rich zone residence time of at least 100 ms, 90 percent TFN reduction can be achieved in the rich zone. Burner design guidelines resulting from this analysis are:

- Fine coal grind (mass mean diameter less than 10 microns).
- For coal injection in lift line, maximum of 20 percent FGR and a high flue gas temperature (~2000°F).
- For coal injection in burner throat, flue gas recirculation to the secondary air.
- Approximately 100 ms residence time in the rich zone (additional rich zone residence time will be obtained in the furnace, prior to the mixing of the secondary combustion air).
- Primary/secondary air flow split approximately 50/50.

4.2.2 One-Dimensional Coal Combustion Modelling

The one-dimensional coal combustion model referred to in Section 4.1 was also used to examine fuel size effects in the rich zone. Six rich zone combustion cases were considered, as detailed in Table 4-3 below.

The results are presented in exactly the same format as the pyrolysis cases discussed in Section 4.1. Cases B1 - B3 have the output from pyrolysis case A3 (at time 200 ms) as their starting point, and cases B4 - B6 have the output from pyrolysis case A4 as their starting point. The results for all six cases are provided in Appendix C. The calculations were continued for 200 ms. The benefits of a fine coal grind can be seen by considering cases B3 and B6, shown in Figures 4-9 and 4-10, respectively:

Case B3. At the end of 200 ms residence time in the rich zone, the mass fraction of unburned char is still very high, at approximately 44 percent. This means that although the global equivalence ratio is approximately 1.8, the gas phase is approximately stoichiometric. Significant unburned char is present in all particles larger than 32 μm . The conditions are therefore not conducive to conversion of TFN to molecular nitrogen.

Cases A3 and B3

Figure 4-9. Pyrolysis and rich zone combustion of reference coal.

Cases A4 and B6

Figure 4-10. Pyrolysis and rich zone combustion of fine coal.

**Table 4-3. Rich Combustion Zone Cases Computed Using
One-Dimensional Combustion Model**

Case	Coal Size	Primary Air (% of Total Air)	Flue Gas Recirculation Rate (%)	Flue Gas Temperature K
B1	Ref (MMD 23 μm)	15	40	1400
B2	Ref (MMD 23 μm)	30	40	1400
B3	Ref (MMD 23 μm)	50	40	1400
B4	Fine (MMD 6 μm)	15	40	1400
B5	Fine (MMD 6 μm)	30	40	1400
B6	Fine (MMD 6 μm)	50	40	1400

Case B6. In the case of the fine coal, more than 90 percent carbon conversion was obtained after only approximately 40 ms. At the end of the calculation (200 ms), the unburned char was only 7 percent (compared to 44 percent for the reference coal), and therefore the gas phase stoichiometry is approximately equal to the global stoichiometry. These temperature and stoichiometry conditions are conducive to TFN destruction. Once again, significant char was left only in particles larger than approximately 30 microns, but for this coal, 90 percent of the mass is contained in particles smaller than this size.

For the case of 40 percent flue gas recirculation and a 50/50 primary/secondary combustion air split, the total time required for a carbon conversion of more than 90 percent was over 200 ms for the utility grind coal and only 40 ms for the fine coal. Thus the utility grind coal combustion in the rich zone is too slow to either produce a rich enough gas-phase stoichiometry for long enough or to release all the fuel nitrogen. The fine coal cases show the potential for essentially complete carbon conversion and nitrogen release in a short enough time to subsequently allow significant conversion of fuel-bound nitrogen to molecular nitrogen.

4.3 Lean Combustion Zone

The MIT analysis for the lean char burnout zone is presented in Appendix D. The MIT analysis suggests the following:

- Burnout time for a 100 μm particle at 5% O_2 is approximately 200 ms.
- The burnout zone will be approximately 18 feet in length for a 100 μm particle.

- The secondary air should be separated into two streams. Approximately 40 percent of the secondary air should be directed into the rich zone exhaust for rapid mixing and combustion. The remaining secondary air should be directed parallel to the rich zone exhaust.

The one-dimensional coal combustion model used for the pyrolysis and rich combustion zone calculations was also used to examine char burnout in the lean zone. The same six cases considered in the rich zone analysis were computed and the results are presented in Appendix E. Secondary combustion air was added (with a characteristic mixing time of 50 ms) and the final combustion process tracked for 500 ms. Figures 4-11 and 4-12 show the results for Cases B3 and B6 respectively. In the case of the fine coal (A4 and B6, Figure 4-12), there is almost no solid fuel left to burn out, and combustion is completed relatively quickly. In the case of the reference coal (A3 and B3, Figure 4-11), the distribution in particle burnout times can be seen in the lower right-hand plot. The largest particles take approximately 500 ms to burn out.

Figure 4-11. Lean zone burnout of reference coal.

Cases A4 and B6 with Final Burnout

Figure 4-12. Lean zone burnout of fine coal.

5 Burner Preliminary Design

The key conclusions from the burner design analyses, which were incorporated into the burner preliminary design, are as follows:

- Coal particle entrainment, heatup and pyrolysis times are short. The coal lift line provides ample residence time and no additional dwell time need be provided between coal injection and the jet pump.
- A fine coal grind is required for rapid burnout in the rich zone, with complete release of fuel-bound nitrogen.
- If the coal is to be injected into the lift line, then the flue gas recirculation rate should be a maximum of 20 percent at 1400 K (2000°F), in order to maximize the temperature in the rich zone.
- If the coal is injected into the burner throat as opposed to being devolatilized by the recirculated flue gas, then the flue gas should be recirculated to the secondary combustion air to provide thermal NO_x control in the lean zone.
- Approximately 100 ms residence time should be provided in the rich zone. Additional rich zone residence time can be provided by delaying mixing of the secondary combustion air in the furnace.
- The primary/secondary airflow split should be approximately 50/50. The primary airflow will be adequate to entrain 20 percent flue gas.

The preliminary design for a 5 MM Btu/hr burner based on the above design principles is shown in Figures 5-1 and 5-2. The flue gas is recirculated in a 7 in ID refractory-lined duct. A primary air pressure drop of approximately 10 in WC is required to entrain 20 percent flue gas at 1400 K (2000°F). The primary air nozzle diameter is 3.22 in, the mixing tube diameter is 5.67 in, and the diffuser exit diameter is 10 in. The rich zone combustion chamber diameter is 18 in and its length is 33 in. The design of the secondary air injection system has not been optimized and is shown schematically in Figures 5-1 and 5-2.

6 Market Evaluation

6.1 Sources of Information

We reviewed industrial coal-use databases to determine the US geographic distribution of industrial coal-fired boilers and furnaces and also the distribution of US coal use by industrial application. We then conducted interviews with representatives of industrial trade associations, coal companies, and industrial coal users to understand important issues for coal selection and use in specific industries. Many of the sources contacted during the review of industrial coal use also provided information useful for the market assessment. A number of additional trade associations were also contacted. Table 6-1 lists the organizations contacted.

Table 6-1. Sources Contacted for Market Evaluation

Group	Sources
Trade Associations	<ul style="list-style-type: none">• CIBO (Council of Industrial Boiler Operators)• Portland Cement Association• National Coal Association• National Lime Association• Glass Technical Institute• American Boiler Manufacturer's Association• Brick Institute of America
Coal Sales	<ul style="list-style-type: none">• AMAX Coal Sales• Consolidated Coal
Coal Database Services	<ul style="list-style-type: none">• Keystone Coal Manual• Resource Data International• Energy Information Agency
Industrial Coal Users	<ul style="list-style-type: none">• Kaiser Cement, CA• PMC, Inc. (Chemicals), OH• Emory Chemicals, OH• Archer Daniels Midland (Food Processing), IL• Campbell's Soup, OH

6.2 Market Drivers

Key factors driving the market for low-NO_x industrial pulverized coal burners are:

- State and Federal emissions regulations.
- Cost differential between coal and gas/oil.

Existing installations in regions that are in non-attainment with the National Ambient Air Quality Standards for ozone or nitrogen oxides will be required to implement RACT (Reasonably Attainable Control Technology) reduce NO_x emissions. New sources or plant expansions in non-attainment areas will be required to meet the LAER (Lowest Achievable Emission Rate) standard. New sources of plant expansions in attainment regions will be required to implement BACT (Best Available Control Technology). As a result of this legislation, regulatory pressure on industrial coal users is increasing.

The most stringent regulations affecting industrial combustion systems are those of the South Coast Air Quality Management District (SCAQMD). For example, all boilers of at least 2 MM Btu/hr input are regulated for NO_x. Rule 1146 restricts NO_x emissions from industrial boilers with heat input capacities of 5 MM Btu/hr or more to 0.05 lb/MM Btu, unless the unit is greater than 40 MM Btu/hr capacity, in which case the limit is 0.04 lb/MM Btu. These limits are possible in Southern California only because of the reliance on natural gas and light distillate oil: coal is effectively excluded by these regulations.

Other regions where increased pressure is likely include Texas, Illinois, Pennsylvania and the Ozone Transport Region (Maine to Virginia). A number of regions are contemplating emissions trading systems (SCAQMD RECLAIM program, Illinois, NESCAUM). A low-cost low-NO_x combustion system will be of premium value in such a trading system, allowing the user to sell NO_x credits.

Figure 6-1 shows the Energy Information Agency (EIA) fuel price projections for natural gas and for coal. After the year 2000 a significant cost premium for natural gas is projected. This will make coal a more attractive fuel, despite its additional emissions control requirements. Those installations which do not require supplemental sulfur and particulate control equipment will likely be the first to adopt the low-NO_x coal burner, followed by larger installations which need sulfur and particulate control equipment (because of economies of scale), and subsequently by smaller installations.

6.3 Potential Markets for Low-NO_x Coal Burner

Potential markets for the low-NO_x coal burner are summarized in Table 6-2. The use of coal in general and of the proposed low-NO_x coal burner specifically in four industrial applications is discussed below. The four are lime kilns, cement kilns, brick kilns and industrial boilers. These applications have the greatest potential among those considered.

Table 6-2. Potential Markets for Low-NO_x Coal-Fired Burner

Application	Approximate Firing Rate (MM Btu/hr)	Inventory of Existing Units	
		Total (Convertible to Coal)	Currently Coal-Fired
Lime kilns	50 - 100	100	90
Cement kilns	100 - 250	230	210
Brick kilns	5 - 10	200 (30 - 50 burners/kiln)	20
Boilers	10 - 100	8,000 (coal)* 16,000 (residual oil)	1000**

* Includes both stoker- and PC-fired units.

** Data from EIA Form 3.

- (1) Based on EIA Annual Energy Outlook 1990 Base Case through 2010, EIA Life-Cycle Base Case costing assumptions through 2040, 0.6% per year escalation thereafter.
- (2) Based on EIA Annual Energy Outlook 1990 Base Case through 2010, EIA Life-Cycle Base Case costing assumptions through 2040, 1.5% per year escalation thereafter.

Figure 6-1. EIA fuel price projections for coal and natural gas.

Lime Kilns

Approximately 18 million tons per year of lime are currently produced in the US. Lime is made in rotary kilns, 95 percent of which are coal-fired. Some 6 million tons per year of coal are consumed in the manufacture of lime. The largest single market for lime is in the steel industry, which consumes some 5 million tons per year. However, use of lime in flue gas desulfurization has grown from 0.6 million tons per year in 1979 to 2 million tons per year in 1989, and is projected to reach 4 million tons per year in 1996. There are approximately 90 large lime plants in 30 states, with concentrations in Missouri, Ohio, Pennsylvania, Texas, Kentucky, Virginia, and Alabama. There are also many small captive lime plants across the country, particularly in the pulp and paper industry.

No additional flue gas desulfurization equipment is needed when burning coal in lime kilns. High temperature flue gas would need to be extracted from around the burner itself. The burner size would likely be in the range 50 - 100 MM Btu/hr.

Cement Kilns

U.S. clinker capacity has held constant at approximately 85 million tons per year for about a decade. There are approximately 230 cement kilns in the U.S., with a trend in the industry to decreasing the number of kilns and increasing the capacity of each kiln. The average kiln capacity in 1988 was 361,000 tons per year. Approximately 94 percent of U.S. cement kilns currently burn coal. NO_x emissions are a concern for the industry: the state with the largest clinker capacity is California.

As with lime kilns, no additional flue gas desulfurization equipment is needed when burning coal in cement kilns. High temperature flue gas would need to be extracted from around the burner itself. The burner size would be larger than for lime kilns, and would likely be in the range 100 - 250 MM Btu/hr.

Brick Kilns

U.S. brick production levels have held steady at approximately 10 billion "standard brick equivalents" per year for the last 30 years. Brick production is concentrated in the South East, the Mid South, Pennsylvania and Ohio. Tunnel kilns of approximately 20 ft x 40 ft cross section are used to fire the bricks. The kiln length can vary from 100 ft to 500 ft and many (30 - 50) small burners are distributed along the kiln.

There are approximately 200 brick kilns in the U.S. Currently only approximately 10 percent are coal fired, with over 70 percent fired by natural gas. However, the industry has a history of coal conversion for improved economics. The low-NO_x coal burner would be more difficult to retrofit to brick kilns, given the number of burners and the additional emissions control equipment required.

Industrial Boilers

The majority of coal-burning industrial boilers are to be found in the chemicals, paper, food and textiles industries. The proposed low-NO_x coal burner has the potential for application in boilers currently firing pulverized coal, residual oil or in stoker-fired boilers. There are approximately 25,000 industrial boilers in the above categories. Figure 6-? shows the distribution of water tube boilers by capacity and fuel type. The pulverized coal units tend to be larger, and are in the range 50 to 250 MM Btu/hr. The majority of the residual oil-fired units are less than 50 MM Btu/hr.

Some of the issues relating to application of the low-NO_x burner in these boilers are that there is a wide range of boiler sizes, with a significant fraction of the population either stoker-fired or residual oil-fired. However, there is a history of fuel switching for economic reasons in industrial boilers. Given the low to moderate process temperature in boilers, there is a requirement for flue gas recirculation from the burner face.

6.4 Conclusions

There is greatest potential for application of the low-NO_x burner in four areas: lime kilns, cement kilns, brick kilns and industrial boilers. Lime and cement kiln applications will require no additional flue gas desulfurization equipment, given the SO₂ capture inherent to the processes. In addition, most of the kilns in the country are already coal-fired. The near term market would be for lime kilns, with burners in the range 50 - 100 MM Btu/hr. The burner can then be scaled up for cement kilns (100 - 250 MM Btu/hr).

In the longer term the burner can be scaled up for larger industrial boilers, i.e. those which already burn coal and/or those in which the economic impact of SO₂ control will cause least hardship. The longest term market will be for small scale industrial boilers, where the relatively higher cost of FGD equipment will dictate a higher fuel price differential before switching to coal is attractive.

ABMA, 1977

Figure 6-2. Distributio.

7 Conclusions

The principal conclusion from this preliminary design and analysis study is that NO_x emissions of below 0.2 lb/MM Btu can indeed be achieved when burning coals with significant fixed nitrogen contents.

The key conclusions from the modelling study were that the following requirements should be met in order to achieve these very low NO_x emissions:

- A fine coal grind (mass mean diameter less than 10 microns) should be used. This will allow rapid burnout and release of fuel-bound nitrogen in the rich zone.
- If the coal is injected into the lift line, the maximum flue gas recirculation rate should be 20 percent and the flue gas temperature should be high (~1400 K, ~2000°F), in order to maximize the temperature in the rich zone and optimize total fixed nitrogen conversion to molecular nitrogen.
- If the coal is injected into the burner throat as opposed to being devolatilized by the recirculated flue gas, then the flue gas should be recirculated to the secondary combustion air to provide thermal NO_x control in the lean zone.
- Approximately 100 ms residence time in the rich zone should be provided. Additional rich zone residence time will be obtained in the furnace, prior to the mixing of the secondary combustion air.
- The primary/secondary air flow split should be approximately 50/50. This will ensure adequate primary air to entrain 20 percent flue gas recirculation, and will ensure rich enough conditions in the primary zone to give good total fixed nitrogen conversion to molecular nitrogen.

A preliminary design for a 5 MM Btu/hr industrial pulverized coal burner has been prepared based on these guidelines. This burner is expected to achieve NO_x emissions of approximately 100 - 150 ppm at 3% O₂.

There is greatest potential for application of the low-NO_x burner in four areas: lime kilns, cement kilns, brick kilns and industrial boilers. The near term market would be for lime kilns, with burners in the range 50 - 100 MM Btu/hr. The burner can then be scaled up for cement kilns (100 - 250 MM Btu/hr). In the longer term the burner can be scaled up for larger industrial boilers and scaled down for brick kilns (5 - 10 MM Btu/hr).

8 References

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Appendix A

Results of One-Dimensional Coal Combustion

Modelling for Pyrolysis Zone

Case A1

Case A2

Input to be tab

ARTHUR D. LITTLE

1-DIM COAL COMBUSTION

Case A3

1-DIM COAL COMBUSTION

ARTHUR D. LITTLE

Input Q to Quit

Flow Time msec

Flow Time msec

Case A4

Case A5

Appendix B

Results of Chemical Kinetics Modelling for Rich Combustion Zone

Rich Combustion Operating Regimes Contours of 90% TFN Reduction

Rich Combustion Operating Regimes Contours of 80% TFN Reduction

Rich Combustion Operating Regimes Contours of 70% TFN Reduction

Rich Combustion Operating Regimes Contours of 50% TFN Reduction

Rich Combustion Operating Regimes Contours of TFN Reduction - 50 ms

Rich Combustion Operating Regimes Contours of TFN Reduction - 100 ms

100 msec Residence Time
60, 50, 40% Primary Air
5:1 Coal Loading
 $TFN_0 = 2000$ ppm

- ◇ 40% FGR @ 1400K
- △ 20% FGR @ 1400K
- 0% FGR

OPER11

Rich Combustion Operating Regimes Contours of TFN Reduction - 200 ms

OPER10

Rich Combustion Operating Regimes Contours of TFN Reduction - 350 ms

Appendix C

Results of One-Dimensional Coal Combustion

Modelling for Rich Combustion Zone

Cases A3 and B1

Cases A3 and B2

Cases A3 and B3

1-DIM COAL COMBUSTION

ARTHUR D. LITTLE

Input Q to Quit

Flow Time (msec)

Flow Time (msec)

Cases A4 and B5

Cases A4 and B6

Appendix D

MIT Char Burnout Analysis

DRAFT

Industrial Pulverized Coal

Low-NO_x Burner

Interim Report

March 1993

Char Burnout

Submitted by:

The Energy Laboratory and Department of Chemical Engineering

Massachusetts Institute of Technology

Cambridge, MA 02139

Introduction

In the January Interim Report we have presented predicted properties for the flow at the exit of the burner diffuser. From these properties we can estimate the resultant char burnout in the downstream furnace. The important properties at the burner diffuser exit are given in Table I. The problem in question is to estimate the burnout time for the char particles and also the residence time in the combustion section of the furnace.

Table I

Burner - Diffuser Exit Properties

Exit Diameter	27 cm
Exit Temperature	1500°C
Exit Mass Flow	
Particulates	32 g/s
Gases	350 g/s
Oxygen Concentration	0%
Gas Density	0.2 kg/m ³
Gas Velocity	30 m/s

Furnace Minimum Residence Time

The combustion time in the furnace is a minimum along the centerline where the velocity is the highest. The velocity is estimated from the turbulent jet correlations of Beér and Chigier⁽¹⁾:

$$\frac{u_o}{u_m} = \frac{1}{6.4} \left\{ \frac{y}{d_o^*} - 1.5 \right\} \quad (1)$$

where u_o is the initial jet velocity, u_m the velocity on axis, y , the distance along axis and d_o^*

the modified burner exit diameter

$$\frac{d_o^*}{d_o} = \left(\frac{\rho_o}{\rho_\infty}\right)^{1/2} \quad (2)$$

where ρ_o is the initial jet density and ρ_∞ is the ambient density.

Equation 1 can be integrated along the centerline to give the residence time as a function of distance, y .

$$t = \frac{d_o^*/u_o}{12.8} \left\{ \left(\frac{y}{d_o^*}\right)^2 - 3\left(\frac{y}{d_o^*}\right) \right\} \quad (3)$$

For the conditions of interest, the ambient temperature is about 1200°C and the mass loading of particulates in the jet is about 10%, so that

$$d_o^* - d_o = 27cm$$

Then

$$t = 7 \times 10^{-4} \left\{ \left(\frac{y}{d_o}\right)^2 - 3\left(\frac{y}{d_o}\right) \right\} \text{ (seconds)} \quad (4)$$

Since the combustor mass flow is proportional to $u_o d_o^2$, for a given mass flow, the residence time will increase as d_o for a fixed length furnace.

Char Combustion Time

The combustion time for char particles can be found from the model of Field et al ⁽²⁾ or from the data correlation of Essenhigh⁽³⁾. The burnout is limited by the larger particles and is

thus a strong function of the grind of the coal. Further, the coal of interest is a swelling coal and the char particles will be about twice the size of the initial coal particles.

The rate of combustion of the char particles can be limited by chemical kinetics or diffusion and can be represented as (mass loss rate per external surface area):

$$g = \frac{P_{O_2}}{\frac{1}{k_{diff}} + \frac{1}{k_s}} \quad (g/cm^2.s) \quad (5)$$

The chemical kinetic rate is found to be:⁽²⁾

$$k_s = 8710 \exp (-17850/T) \quad g/cm^2.s.atm \quad (6)$$

and the diffusion rate:

$$k_{diff} = 9.4 \times 10^{-4} \left(\frac{T}{1000} \right)^{3/4} \frac{1}{d(cm)}, \quad g/cm^2.s \quad atm \quad (7)$$

These rates are about equal for a $d = 100 \mu m$ particle at $1300^\circ C$. At higher temperatures or for larger particles, the diffusion rate dominates. Since we are interested in the burnout of the larger particles, the diffusion rate is assumed to dominate. This can be seen from the data correlation of Essenhigh⁽³⁾ (see Figure 1).

We can select the combustion temperature of $1200^\circ C$ for the particles from typical furnace properties and calculate the combustion time by using a char density of $0.5 g/cm^3$ and assuming a shrinking sphere model (surface burning) for the combustion. The burnout time is found by integrating the char diameter to zero:

$$t = \frac{\rho_s d^2/4}{P_{O_2} 9.4 \times 10^{-4} \left(\frac{T}{1000}\right)^{3/4}} \quad (8)$$

which at 1500 K corresponds to

$$t = \frac{1 \times 10^{-2}}{P_{O_2}} \left(\frac{d(\mu m)}{100}\right)^2 \quad (9)$$

If the oxygen concentration can be held to 5% or greater in the burnout region then the combustion time will be

$$t = 0.2 \left(\frac{d(\mu m)}{100}\right)^2 \quad (10)$$

Here $d(\mu m)$ is the initial char particle diameter in microns. For a 100 μm char particle (initially 50 μm coal particle). The burnout time is thus 0.2 seconds. This is the same time found from the correlation presented by Essenhigh⁽³⁾ and shown in Figure 1.

Combustion Length for Char Burnout

The results of Equations 4 and 10 can be combined to provide a minimum combustion length for a given particle size. These equations are presented in the nomograph of Figure 2. From this figure we see that for the 100 μm char particle, the burnout length is 18 ft. This length would be decreased for a larger burner exit diameter at constant mass flow.

The combustion lengths calculated from these relations are not unreasonable. The main furnace section of the CRF is about 18 ft long.

Air Injection

The remaining issue is then the air injectors. The bulk of the combustion air is added after the burner diffuser in the overfire section. The burner exit has a total mass flow of $7.87 \dot{m}_{coal}$ at 1500°C of which $0.66 \dot{m}_{coal}$ is char. The overfire air mass flow is about $6 \dot{m}_{coal}$ at 590°C . The resultant temperature of these flows if rapidly mixed would be too cold for char burnout. An initial rapid mixing of a portion of the overfire air should provide the compromise 5% O_2 . If the burner gases are initially diluted with air flow of $2.4 \dot{m}_{coal}$, (40% of the overfire air), then we reach 5% O_2 at about 1300°C . This is a good temperature for char burnout. The temperature will rise as the char burns but then additional air should be added for burnout. The remaining air ($\dot{m}_{air} / \dot{m}_{coal} = 3.6$) should thus be entrained into the coal jet over the rear part of the furnace.

If the overfire air jets are divided into two types, this can be accomplished. One half of the jets with 40% of the overfire air would be impinging at a sharp angle into the burner exhaust for rapid mixing. The remaining air jets would be close to the burner exhaust and parallel to it. The design air jet diameter of 1 inch will entrain its own mass flow in 3 inches and the burner mass flow in about 12 inches. This is an appropriate size for the impinging jets (at say 45° to horizontal).

The remaining jets should be adjusted in size and placed so that they entrain over the burnout distance of the mean particle size (~ 5 ft.). This is close to the natural entrainment distance for the burner exit and thus will occur naturally unless some extra effort is made. So the close in parallel jet design is appropriate. A larger diameter (2") makes these air jets and the burner exhaust of nearly equal velocity. This is judged appropriate for the desired mixing length.

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Fig. 1 - Variation of Combustion Time with Particle Diameter from Various Experimental and Theoretical Sources.

FIGURE MEMORANDUM FOR BURNOUT OF CHAR
IN FURNACE

$$T = 15 \text{ sec} = 0.25 \text{ min}$$

$$\rho_{\text{char}} = 0.95 \text{ g/cm}^3$$

BURNOUT TIME

FURNACE RESIDENCE TIME

$$\rho_{\text{char}}/\rho_{\text{ash}} = 0.95 \text{ g/cm}^3$$

$$\rho_{\text{char}}/\rho_{\text{ash}} = 0.95 \text{ g/cm}^3$$

$d(\mu\text{m})$

Time (seconds)

$d_0 = 200 \mu\text{m}$

$d(\mu\text{m})$

$d_0 = 200 \mu\text{m}$

AIM

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Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

2 of 2

Appendix E

Results of One-Dimensional Coal Combustion

Modelling for Lean Burnout Zone

Cases A3 and B1 with Final Burnout

Cases A3 and B2 with Final Burnout

Cases A3 and B3 with Final Burnout

Cases A4 and B4 with Final Burnout

Cases A4 and B5 with Final Burnout

Cases A4 and B6 with Final Burnout

Cases A4 and B6 with Final Burnout (3% O₂)

Appendix F

Species and Reactions Considered in Chemical Kinetics Analyses

Species and Reactions Considered in Chemical Kinetics Analyses

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 2.8 Jun. 1991
DOUBLE PRECISION

ELEMENTS CONSIDERED	ATOMIC WEIGHT
1. H	1.00797
2. O	15.9994
3. C	12.0112
4. N	14.0067

SPECIES CONSIDERED	S E	G E	MOLECULAR WEIGHT	TEMPERATURE		ELEMENT COUNT			
				LOW	HIGH	H	O	C	N
1. CH4	G	0	16.04303	300.0	5000.0	4	0	1	0
2. CH3	G	0	15.03506	300.0	5000.0	3	0	1	0
3. CH2	G	0	14.02709	250.0	4000.0	2	0	1	0
4. CH	G	0	13.01912	300.0	5000.0	1	0	1	0
5. CH2O	G	0	30.02649	300.0	5000.0	2	1	1	0
6. HCO	G	0	29.01852	300.0	5000.0	1	1	1	0
7. CO2	G	0	44.00995	300.0	5000.0	0	2	1	0
8. CO	G	0	28.01055	300.0	5000.0	0	1	1	0
9. H2	G	0	2.01594	300.0	5000.0	2	0	0	0
10. H	G	0	1.00797	300.0	5000.0	1	0	0	0
11. O2	G	0	31.99880	300.0	5000.0	0	2	0	0
12. O	G	0	15.99940	300.0	5000.0	0	1	0	0
13. OH	G	0	17.00737	300.0	5000.0	1	1	0	0
14. HO2	G	0	33.00677	300.0	5000.0	1	2	0	0
15. H2O2	G	0	34.01474	300.0	5000.0	2	2	0	0
16. H2O	G	0	18.01534	300.0	5000.0	2	1	0	0
17. C2H	G	0	25.03027	300.0	5000.0	1	0	2	0
18. C2H2	G	0	26.03824	300.0	5000.0	2	0	2	0
19. HCCO	G	0	41.02967	300.0	4000.0	1	1	2	0
20. C2H3	G	0	27.04621	300.0	5000.0	3	0	2	0
21. C2H4	G	0	28.05418	300.0	5000.0	4	0	2	0
22. C2H5	G	0	29.06215	300.0	5000.0	5	0	2	0
23. C2H6	G	0	30.07012	300.0	4000.0	6	0	2	0
24. CH2OH	G	0	31.03446	250.0	4000.0	3	1	1	0
25. CH3O	G	0	31.03446	300.0	3000.0	3	1	1	0
26. H2CCCH	G	0	39.05736	300.0	4000.0	3	0	3	0
27. C3H2	G	0	38.04939	300.0	5000.0	2	0	3	0
28. CH2(S)	G	0	14.02709	300.0	4000.0	2	0	1	0
29. CH2CO	G	0	42.03764	300.0	5000.0	2	1	2	0
30. C	G	0	12.01115	300.0	5000.0	0	0	1	0
31. C4H2	G	0	50.06054	300.0	5000.0	2	0	4	0
32. H2CCCCH	G	0	51.06851	300.0	4000.0	3	0	4	0
33. HCCOH	G	0	42.03764	300.0	4000.0	2	1	2	0

34. N2	G 0	28.01340	300.0	5000.0	0	0	0	2
35. NO	G 0	30.00610	300.0	5000.0	0	1	0	1
36. N	G 0	14.00670	300.0	5000.0	0	0	0	1
37. NH	G 0	15.01467	300.0	5000.0	1	0	0	1
38. NH2	G 0	16.02264	300.0	5000.0	2	0	0	1
39. HNO	G 0	31.01407	300.0	5000.0	1	1	0	1
40. HCN	G 0	27.02582	300.0	5000.0	1	0	1	1
41. NCO	G 0	42.01725	300.0	5000.0	0	1	1	1
42. CN	G 0	26.01785	300.0	5000.0	0	0	1	1
43. N2O	G 0	44.01280	300.0	5000.0	0	1	0	2
44. NNH	G 0	29.02137	250.0	4000.0	1	0	0	2
45. HNCO	G 0	43.02522	300.0	4000.0	1	1	1	1
46. C2N2	G 0	52.03570	300.0	5000.0	0	0	2	2
47. NO2	G 0	46.00550	300.0	5000.0	0	2	0	1
48. HOCN	G 0	43.02522	250.0	4000.0	1	1	1	1
49. HCNO	G 0	43.02522	250.0	4000.0	1	1	1	1
50. H2CN	G 0	28.03379	300.0	4000.0	2	0	1	1
51. NH3	G 0	17.03061	300.0	5000.0	3	0	0	1

REACTIONS CONSIDERED			(k = A T**b exp(-E/RT))		
			A	b	E
1. CH3+CH3 (+M)=C2H6 (+M)			9.03E+16	-1.2	654.0
Low pressure limit:	0.31800E+42	-0.70300E+01	0.27620E+04		
TROE centering:	0.60410E+00	0.69270E+04	0.13200E+03		
H2	Enhanced by	2.000E+00			
CO	Enhanced by	2.000E+00			
CO2	Enhanced by	3.000E+00			
H2O	Enhanced by	5.000E+00			
2. CH3+H (+M)=CH4 (+M)			6.00E+16	-1.0	0.0
Low pressure limit:	0.80000E+27	-0.30000E+01	0.00000E+00		
SRI centering:	0.45000E+00	0.79700E+03	0.97900E+03		
H2	Enhanced by	2.000E+00			
CO	Enhanced by	2.000E+00			
CO2	Enhanced by	3.000E+00			
H2O	Enhanced by	5.000E+00			
3. CH4+O2=CH3+HO2			7.90E+13	0.0	56000.0
4. CH4+H=CH3+H2			2.20E+04	3.0	8750.0
5. CH4+OH=CH3+H2O			1.60E+06	2.1	2460.0
6. CH4+HO2=CH3+H2O2			1.80E+11	0.0	18700.0
7. CH3+HO2=CH3O+OH			2.00E+13	0.0	0.0
8. CH3+O2=CH3O+O			2.05E+18	-1.6	29229.0
9. CH3+O=CH2O+H			8.00E+13	0.0	0.0
10. CH2OH+H=CH3+OH			1.00E+14	0.0	0.0
11. CH3O+H=CH3+OH			1.00E+14	0.0	0.0
12. CH3+OH=CH2+H2O			7.50E+06	2.0	5000.0
13. CH3+H=CH2+H2			9.00E+13	0.0	15100.0
14. CH3O+M=CH2O+H+M			1.00E+14	0.0	25000.0
15. CH2OH+M=CH2O+H+M			1.00E+14	0.0	25000.0
16. CH3O+H=CH2O+H2			2.00E+13	0.0	0.0
17. CH2OH+H=CH2O+H2			2.00E+13	0.0	0.0
18. CH3O+OH=CH2O+H2O			1.00E+13	0.0	0.0
19. CH2OH+OH=CH2O+H2O			1.00E+13	0.0	0.0
20. CH3O+O=CH2O+OH			1.00E+13	0.0	0.0
21. CH2OH+O=CH2O+OH			1.00E+13	0.0	0.0
22. CH3O+O2=CH2O+HO2			6.30E+10	0.0	2600.0
23. CH2OH+O2=CH2O+HO2			1.48E+13	0.0	1500.0
24. CH2+H=CH+H2			1.00E+18	-1.6	0.0
25. CH2+OH=CH+H2O			1.13E+07	2.0	3000.0

26.	CH ₂ +OH=CH ₂ O+H	2.50E+13	0.0	0.0
27.	CH+O ₂ =HCO+O	3.30E+13	0.0	0.0
28.	CH+O=CO+H	5.70E+13	0.0	0.0
29.	CH+OH=HCO+H	3.00E+13	0.0	0.0
30.	CH+CO ₂ =HCO+CO	3.40E+12	0.0	690.0
31.	CH+H=C+H ₂	1.50E+14	0.0	0.0
32.	CH+H ₂ O=CH ₂ O+H	1.17E+15	-0.8	0.0
33.	CH+CH ₂ O=CH ₂ CO+H	9.46E+13	0.0	-515.0
34.	CH+C ₂ H ₂ =C ₃ H ₂ +H	1.00E+14	0.0	0.0
35.	CH+CH ₂ =C ₂ H ₂ +H	4.00E+13	0.0	0.0
36.	CH+CH ₃ =C ₂ H ₃ +H	3.00E+13	0.0	0.0
37.	CH+CH ₄ =C ₂ H ₄ +H	6.00E+13	0.0	0.0
38.	C+O ₂ =CO+O	2.00E+13	0.0	0.0
39.	C+OH=CO+H	5.00E+13	0.0	0.0
40.	C+CH ₃ =C ₂ H ₂ +H	5.00E+13	0.0	0.0
41.	C+CH ₂ =C ₂ H+H	5.00E+13	0.0	0.0
42.	CH ₂ +CO ₂ =CH ₂ O+CO	1.10E+11	0.0	1000.0
43.	CH ₂ +O=CO+H+H	5.00E+13	0.0	0.0
44.	CH ₂ +O=CO+H ₂	3.00E+13	0.0	0.0
45.	CH ₂ +O ₂ =CO ₂ +H+H	1.60E+12	0.0	1000.0
46.	CH ₂ +O ₂ =CH ₂ O+O	5.00E+13	0.0	9000.0
47.	CH ₂ +O ₂ =CO ₂ +H ₂	6.90E+11	0.0	500.0
48.	CH ₂ +O ₂ =CO+H ₂ O	1.90E+10	0.0	-1000.0
49.	CH ₂ +O ₂ =CO+OH+H	8.60E+10	0.0	-500.0
50.	CH ₂ +O ₂ =HCO+OH	4.30E+10	0.0	-500.0
51.	CH ₂ O+OH=HCO+H ₂ O	3.43E+09	1.2	-447.0
52.	CH ₂ O+H=HCO+H ₂	2.19E+08	1.8	3000.0
53.	CH ₂ O+M=HCO+H+M	3.31E+16	0.0	81000.0
54.	CH ₂ O+O=HCO+OH	1.80E+13	0.0	3080.0
55.	HCO+OH=H ₂ O+CO	1.00E+14	0.0	0.0
56.	HCO+M=H+CO+M	2.50E+14	0.0	16802.0
	CO	Enhanced by	1.870E+00	
	H ₂	Enhanced by	1.870E+00	
	CH ₄	Enhanced by	2.810E+00	
	CO ₂	Enhanced by	3.000E+00	
	H ₂ O	Enhanced by	5.000E+00	
57.	HCO+H=CO+H ₂	1.19E+13	0.2	0.0
58.	HCO+O=CO+OH	3.00E+13	0.0	0.0
59.	HCO+O=CO ₂ +H	3.00E+13	0.0	0.0
60.	HCO+O ₂ =HO ₂ +CO	3.30E+13	-0.4	0.0
61.	CO+O+M=CO ₂ +M	6.17E+14	0.0	3000.0
62.	CO+OH=CO ₂ +H	1.51E+07	1.3	-758.0
63.	CO+O ₂ =CO ₂ +O	2.53E+12	0.0	47688.0
64.	HO ₂ +CO=CO ₂ +OH	5.80E+13	0.0	22934.0
65.	C ₂ H ₆ +CH ₃ =C ₂ H ₅ +CH ₄	5.50E-01	4.0	8300.0
66.	C ₂ H ₆ +H=C ₂ H ₅ +H ₂	5.40E+02	3.5	5210.0
67.	C ₂ H ₆ +O=C ₂ H ₅ +OH	3.00E+07	2.0	5115.0
68.	C ₂ H ₆ +OH=C ₂ H ₅ +H ₂ O	8.70E+09	1.1	1810.0
69.	C ₂ H ₄ +H=C ₂ H ₃ +H ₂	1.10E+14	0.0	8500.0
70.	C ₂ H ₄ +O=CH ₃ +HCO	1.60E+09	1.2	746.0
71.	C ₂ H ₄ +OH=C ₂ H ₃ +H ₂ O	2.02E+13	0.0	5955.0
72.	CH ₂ +CH ₃ =C ₂ H ₄ +H	3.00E+13	0.0	0.0
73.	H+C ₂ H ₄ (+M)=C ₂ H ₅ (+M)	2.21E+13	0.0	2066.0
	Low pressure limit:	0.63690E+28	-0.27600E+01	-0.54000E+02
	H ₂	Enhanced by	2.000E+00	
	CO	Enhanced by	2.000E+00	
	CO ₂	Enhanced by	3.000E+00	
	H ₂ O	Enhanced by	5.000E+00	
74.	C ₂ H ₅ +H=CH ₃ +CH ₃	1.00E+14	0.0	0.0
75.	C ₂ H ₅ +O ₂ =C ₂ H ₄ +HO ₂	8.43E+11	0.0	3875.0
76.	C ₂ H ₂ +O=CH ₂ +CO	1.02E+07	2.0	1900.0
77.	C ₂ H ₂ +O=HCCO+H	1.02E+07	2.0	1900.0

78.	$H_2 + C_2H = C_2H_2 + H$		4.09E+05	2.4	864.3
79.	$H + C_2H_2 (+M) = C_2H_3 (+M)$		5.54E+12	0.0	2410.0
	Low pressure limit:	0.26700E+28 -0.35000E+01	0.24100E+04		
	H ₂	Enhanced by	2.000E+00		
	CO	Enhanced by	2.000E+00		
	CO ₂	Enhanced by	3.000E+00		
	H ₂ O	Enhanced by	5.000E+00		
80.	$C_2H_3 + H = C_2H_2 + H_2$		4.00E+13	0.0	0.0
81.	$C_2H_3 + O = CH_2CO + H$		3.00E+13	0.0	0.0
82.	$C_2H_3 + O_2 = CH_2O + HCO$		4.00E+12	0.0	-250.0
83.	$C_2H_3 + OH = C_2H_2 + H_2O$		5.00E+12	0.0	0.0
84.	$C_2H_3 + CH_2 = C_2H_2 + CH_3$		3.00E+13	0.0	0.0
85.	$C_2H_3 + C_2H = C_2H_2 + C_2H_2$		3.00E+13	0.0	0.0
86.	$C_2H_3 + CH = CH_2 + C_2H_2$		5.00E+13	0.0	0.0
87.	$OH + C_2H_2 = C_2H + H_2O$		3.37E+07	2.0	14000.0
88.	$OH + C_2H_2 = HCCOH + H$		5.04E+05	2.3	13500.0
89.	$OH + C_2H_2 = CH_2CO + H$		2.18E-04	4.5	-1000.0
90.	$OH + C_2H_2 = CH_3 + CO$		4.83E-04	4.0	-2000.0
91.	$HCCOH + H = CH_2CO + H$		1.00E+13	0.0	0.0
92.	$C_2H_2 + O = C_2H + OH$		3.16E+15	-0.6	15000.0
93.	$CH_2CO + O = CO_2 + CH_2$		1.75E+12	0.0	1350.0
94.	$CH_2CO + H = CH_3 + CO$		1.13E+13	0.0	3428.0
95.	$CH_2CO + H = HCCO + H_2$		5.00E+13	0.0	8000.0
96.	$CH_2CO + O = HCCO + OH$		1.00E+13	0.0	8000.0
97.	$CH_2CO + OH = HCCO + H_2O$		7.50E+12	0.0	2000.0
98.	$CH_2CO (+M) = CH_2 + CO (+M)$		3.00E+14	0.0	70980.0
	Low pressure limit:	0.36000E+16 0.00000E+00	0.59270E+05		
99.	$C_2H + O_2 = CO + CO + H$		5.00E+13	0.0	1500.0
100.	$C_2H + C_2H_2 = C_4H_2 + H$		3.00E+13	0.0	0.0
101.	$H + HCCO = CH_2 (S) + CO$		1.00E+14	0.0	0.0
102.	$O + HCCO = H + CO + CO$		1.00E+14	0.0	0.0
103.	$HCCO + O_2 = CO + CO + OH$		1.60E+12	0.0	854.0
104.	$CH + HCCO = C_2H_2 + CO$		5.00E+13	0.0	0.0
105.	$HCCO + HCCO = C_2H_2 + CO + CO$		1.00E+13	0.0	0.0
106.	$CH_2 (S) + M = CH_2 + M$		1.00E+13	0.0	0.0
	H	Enhanced by	0.000E+00		
107.	$CH_2 (S) + CH_4 = CH_3 + CH_3$		4.00E+13	0.0	0.0
108.	$CH_2 (S) + C_2H_6 = CH_3 + C_2H_5$		1.20E+14	0.0	0.0
109.	$CH_2 (S) + O_2 = CO + OH + H$		3.00E+13	0.0	0.0
110.	$CH_2 (S) + H_2 = CH_3 + H$		7.00E+13	0.0	0.0
111.	$CH_2 (S) + H = CH_2 + H$		2.00E+14	0.0	0.0
112.	$C_2H + O = CH + CO$		5.00E+13	0.0	0.0
113.	$C_2H + OH = HCCO + H$		2.00E+13	0.0	0.0
114.	$CH_2 + CH_2 = C_2H_2 + H_2$		4.00E+13	0.0	0.0
115.	$CH_2 + HCCO = C_2H_3 + CO$		3.00E+13	0.0	0.0
116.	$CH_2 + C_2H_2 = H_2CCCH + H$		1.20E+13	0.0	6600.0
117.	$C_4H_2 + OH = C_3H_2 + HCO$		6.66E+12	0.0	-410.0
118.	$C_3H_2 + O_2 = HCO + HCCO$		1.00E+13	0.0	0.0
119.	$H_2CCCH + O_2 = CH_2CO + HCO$		3.00E+10	0.0	2868.0
120.	$H_2CCCH + O = CH_2O + C_2H$		2.00E+13	0.0	0.0
121.	$H_2CCCH + OH = C_3H_2 + H_2O$		2.00E+13	0.0	0.0
122.	$C_2H_2 + C_2H_2 = H_2CCCH + H$		2.00E+12	0.0	45900.0
123.	$H_2CCCH + M = C_4H_2 + H + M$		1.00E+16	0.0	59700.0
124.	$CH_2 (S) + C_2H_2 = H_2CCCH + H$		3.00E+13	0.0	0.0
125.	$C_4H_2 + O = C_3H_2 + CO$		1.20E+12	0.0	0.0
126.	$C_2H_2 + O_2 = HCCO + OH$		2.00E+08	1.5	30100.0
127.	$C_2H_2 + M = C_2H + H + M$		4.20E+16	0.0	107000.0
128.	$C_2H_4 + M = C_2H_2 + H_2 + M$		1.50E+15	0.0	55800.0
129.	$C_2H_4 + M = C_2H_3 + H + M$		1.40E+16	0.0	82360.0
130.	$H_2 + O_2 = 2OH$		1.70E+13	0.0	47780.0
131.	$OH + H_2 = H_2O + H$		1.17E+09	1.3	3626.0
132.	$O + OH = O_2 + H$		4.00E+14	-0.5	0.0

133.	O+H2=OH+H		5.06E+04	2.7	6290.0
134.	H+O2+M=HO2+M		3.61E+17	-0.7	0.0
	H2O	Enhanced by	1.860E+01		
	CO2	Enhanced by	4.200E+00		
	H2	Enhanced by	2.860E+00		
	CO	Enhanced by	2.110E+00		
	N2	Enhanced by	1.260E+00		
135.	OH+HO2=H2O+O2		7.50E+12	0.0	0.0
136.	H+HO2=2OH		1.40E+14	0.0	1073.0
137.	O+HO2=O2+OH		1.40E+13	0.0	1073.0
138.	2OH=O+H2O		6.00E+08	1.3	0.0
139.	H+H+M=H2+M		1.00E+18	-1.0	0.0
	H2	Enhanced by	0.000E+00		
	H2O	Enhanced by	0.000E+00		
	CO2	Enhanced by	0.000E+00		
140.	H+H+H2=H2+H2		9.20E+16	-0.6	0.0
141.	H+H+H2O=H2+H2O		6.00E+19	-1.2	0.0
142.	H+H+CO2=H2+CO2		5.49E+20	-2.0	0.0
143.	H+OH+M=H2O+M		1.60E+22	-2.0	0.0
	H2O	Enhanced by	5.000E+00		
144.	H+O+M=OH+M		6.20E+16	-0.6	0.0
	H2O	Enhanced by	5.000E+00		
145.	O+O+M=O2+M		1.89E+13	0.0	-1788.0
146.	H+HO2=H2+O2		1.25E+13	0.0	0.0
147.	HO2+HO2=H2O2+O2		2.00E+12	0.0	0.0
148.	H2O2+M=OH+OH+M		1.30E+17	0.0	45500.0
149.	H2O2+H=HO2+H2		1.60E+12	0.0	3800.0
150.	H2O2+OH=H2O+HO2		1.00E+13	0.0	1800.0
151.	CH+N2=HCN+N		3.00E+11	0.0	13600.0
152.	CN+N=C+N2		1.04E+15	-0.5	0.0
153.	CH2+N2=HCN+NH		1.00E+13	0.0	74000.0
154.	H2CN+N=N2+CH2		2.00E+13	0.0	0.0
155.	H2CN+M=HCN+H+M		3.00E+14	0.0	22000.0
156.	C+NO=CN+O		6.60E+13	0.0	0.0
157.	CH+NO=HCN+O		1.10E+14	0.0	0.0
158.	CH2+NO=HCNO+H		1.39E+12	0.0	-1100.0
159.	CH3+NO=HCN+H2O		1.00E+11	0.0	15000.0
160.	CH3+NO=H2CN+OH		1.00E+11	0.0	15000.0
161.	HCCO+NO=HCNO+CO		2.00E+13	0.0	0.0
162.	CH2(S)+NO=HCN+OH		2.00E+13	0.0	0.0
163.	HCNO+H=HCN+OH		1.00E+14	0.0	12000.0
164.	CH2+N=HCN+H		5.00E+13	0.0	0.0
165.	CH+N=CN+H		1.30E+13	0.0	0.0
166.	CO2+N=NO+CO		1.90E+11	0.0	3400.0
167.	HCCO+N=HCN+CO		5.00E+13	0.0	0.0
168.	CH3+N=H2CN+H		3.00E+13	0.0	0.0
169.	C2H3+N=HCN+CH2		2.00E+13	0.0	0.0
170.	H2CCCH+N=HCN+C2H2		1.00E+13	0.0	0.0
171.	HCN+OH=CN+H2O		1.45E+13	0.0	10929.0
172.	OH+HCN=HOCN+H		5.85E+04	2.4	12500.0
173.	OH+HCN=HNCO+H		1.98E-03	4.0	1000.0
174.	OH+HCN=NH2+CO		7.83E-04	4.0	4000.0
175.	HOCN+H=HNCO+H		1.00E+13	0.0	0.0
176.	HCN+O=NCO+H		1.38E+04	2.6	4980.0
177.	HCN+O=NH+CO		3.45E+03	2.6	4980.0
178.	HCN+O=CN+OH		2.70E+09	1.6	29200.0
179.	CN+H2=HCN+H		2.95E+05	2.5	2237.0
180.	CN+O=CO+N		1.80E+13	0.0	0.0
181.	CN+O2=NCO+O		5.60E+12	0.0	0.0
182.	CN+OH=NCO+H		6.00E+13	0.0	0.0
183.	CN+HCN=C2N2+H		2.00E+13	0.0	0.0
184.	CN+NO2=NCO+NO		3.00E+13	0.0	0.0

185.	CN+N2O=NCO+N2	1.00E+13	0.0	0.0
186.	C2N2+O=NCO+CN	4.57E+12	0.0	8880.0
187.	C2N2+OH=HOCN+CN	1.86E+11	0.0	2900.0
188.	HO2+NO=NO2+OH	2.11E+12	0.0	-479.0
189.	NO2+H=NO+OH	3.50E+14	0.0	1500.0
190.	NO2+O=NO+O2	1.00E+13	0.0	600.0
191.	NO2+M=NO+O+M	1.10E+16	0.0	66000.0
192.	NCO+H=NH+CO	5.00E+13	0.0	0.0
193.	NCO+O=NO+CO	2.00E+13	0.0	0.0
194.	NCO+N=N2+CO	2.00E+13	0.0	0.0
195.	NCO+OH=NO+HCO	1.00E+12	0.0	20000.0
196.	NCO+M=N+CO+M	3.10E+16	-0.5	48000.0
197.	NCO+NO=N2O+CO	1.00E+13	0.0	-390.0
198.	NCO+H2=HNCO+H	8.58E+12	0.0	9000.0
199.	HNCO+H=NH2+CO	9.39E+04	2.5	8000.0
200.	HNCO+M=NH+CO	1.14E+16	0.0	86000.0
201.	HNCO+NH=NH2+NCO	3.00E+13	0.0	23700.0
202.	HNCO+NH2=NH3+NCO	5.00E+12	0.0	6200.0
203.	OH+HNCO=NCO+H2O	2.65E+12	0.0	5540.0
204.	HNCO+O=HNO+CO	3.25E+12	0.0	10300.0
205.	NH+O2=HNO+O	1.00E+13	0.0	12000.0
206.	NH+O2=NO+OH	7.60E+10	0.0	1530.0
207.	NH+NO=N2O+H	2.40E+15	-0.8	0.0
208.	N2O+OH=N2+HO2	2.00E+12	0.0	10000.0
209.	N2O+H=N2+OH	7.60E+13	0.0	15200.0
210.	N2O+M=N2+O+M	1.60E+14	0.0	51600.0
211.	N2O+O=N2+O2	1.00E+14	0.0	28200.0
212.	N2O+O=NO+NO	1.00E+14	0.0	28200.0
213.	NH+OH=HNO+H	2.00E+13	0.0	0.0
214.	NH+OH=N+H2O	5.00E+11	0.5	2000.0
215.	NH+N=N2+H	3.00E+13	0.0	0.0
216.	NH+H=N+H2	1.00E+14	0.0	0.0
217.	NH2+O=HNO+H	6.63E+14	-0.5	0.0
218.	NH2+O=NH+OH	6.75E+12	0.0	0.0
219.	NH2+OH=NH+H2O	4.00E+06	2.0	1000.0
220.	NH2+H=NH+H2	6.92E+13	0.0	3650.0
221.	NH2+NO=NNH+OH	6.40E+15	-1.2	0.0
222.	NH2+NO=N2+H2O	6.20E+15	-1.2	0.0
223.	NH3+OH=NH2+H2O	2.04E+06	2.0	566.0
224.	NH3+H=NH2+H2	6.36E+05	2.4	10171.0
225.	NH3+O=NH2+OH	2.10E+13	0.0	9000.0
226.	NNH=N2+H	1.00E+04	0.0	0.0
227.	NNH+NO=N2+HNO	5.00E+13	0.0	0.0
228.	NNH+H=N2+H2	1.00E+14	0.0	0.0
229.	NNH+OH=N2+H2O	5.00E+13	0.0	0.0
230.	NNH+NH2=N2+NH3	5.00E+13	0.0	0.0
231.	NNH+NH=N2+NH2	5.00E+13	0.0	0.0
232.	NNH+O=N2O+H	1.00E+14	0.0	0.0
233.	HNO+M=H+NO+M	1.50E+16	0.0	48680.0
	H2O	Enhanced by	1.000E+01	
	O2	Enhanced by	2.000E+00	
	N2	Enhanced by	2.000E+00	
	H2	Enhanced by	2.000E+00	
234.	HNO+OH=NO+H2O	3.60E+13	0.0	0.0
235.	HNO+H=H2+NO	5.00E+12	0.0	0.0
236.	HNO+NH2=NH3+NO	2.00E+13	0.0	1000.0
237.	N+NO=N2+O	3.27E+12	0.3	0.0
238.	N+O2=NO+O	6.40E+09	1.0	6280.0
239.	N+OH=NO+H	3.80E+13	0.0	0.0
240.	CH4+O=CH3+OH	1.02E+09	1.5	8604.0

NOTE: A units mole-cm-sec-K, E units cal/mole

**DATE
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10 / 7 / 94

END